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Baltica

BALTICA Volume 33 Number 1 June 2020: 21–34

<https://doi.org/10.5200/baltica.2020.1.3>

Seasonal variability in the supply of dissolved matter to catchments of basins without outlets in northern Poland, measured by selected physicochemical indicators

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Cieśliński, R., Major, M., Pietruszyński, L. 2020. Seasonal variability in the supply of dissolved matter to catchments of basins without outlets in northern Poland, measured by selected physicochemical indicators. *Baltica*, 33 (1), 21–34. Vilnius. ISSN 0067-3064.

Manuscript submitted 24 April 2019 / Accepted 30 March 2020 / Published online 25 June 2020

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Abstract. The aim of the study is to determine the seasonal variability in the size of dissolved matter supplied to selected kettle ponds located in the glacial areas of northern Poland, using selected physicochemical indicators. The study area consisted of the drainage basin of the Parsęta River and a small catchment of the Borucinka River that flows across the Kaszubskie Lake District in northern Poland. Measurements of pH, electrolytic conductivity, oxygenation, and water temperature were performed in the field. The concentration of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^- , NH_4^+ , NO_3^- , PO_4^{3-} was measured in the laboratory. Also, the atmospheric precipitation was determined using automatic precipitation stations. Climate conditions served as the primary determinants of seasonal change in the supply of dissolved matter to basins without outlets in the drainage basin. This is especially true of atmospheric precipitation and the effects of vegetation in the contact zone between precipitation and the biosphere. In the case of biogenic substances, one of the main factors was the length of the vegetation season. The main determinant of the hydrochemical state of kettle ponds was land use.

Keywords: northern Poland; plateau levels; basins without outlets; seasonal variances; dissolved matter; ions

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INTRODUCTION

Kettle ponds are commonly found in areas embraced by the last Pleistocene glaciations. They are a natural element of the landscape; together with their closed drainage basins they occupy a large proportion of the area (Marks *et al.* 2016). They play an important role in water retention, aquatic products supply, and biodiversity conservation (Fu *et al.* 2018). One of the more typical features of the hydrography in this geographic area (lake districts) is the occurrence of a very large number of small depressions or kettle ponds (De Meester *et al.* 2005; Biggs *et al.* 2005). They are related to the substitution of the Pleistocene landscape of fluvial and aeolian deposits by periods of marsh growth, brackish semi-enclosed lakes

and tidal flats until a permanent connection with the sea was established (Troelstra *et al.* 2018).

The number of kettle ponds in Poland is estimated to be in the hundreds of thousands. Kettle ponds represent a very important feature in geographic space due to their ability to store water (Major 2012; Cieśliński, Jokiel 2017), as well as to play a number of other roles in hydrology (Oertli *et al.* 2005). These roles will become more and more important, as the increase of atmospheric precipitation resulting from climate change is expected (Fang *et al.* 2017). It can cause the global scarcity of freshwater, which has been gearing towards an unsustainable river basin management and corresponding services to the humans (Srinivas *et al.* 2018). This also applies to small lake reservoirs (Terasmaa *et al.* 2016). Downing (2010) was able to show that kettle ponds play

an important role in the water circulation not only on a regional scale, but also on a global scale. Though kettle ponds are very common, they have not been studied extensively in terms of hydrology.

Very little is known about the hydrochemistry of kettle ponds. Given the morphometry of kettle ponds, specific geo-ecological conditions (Davis *et al.* 2008; Oertli *et al.* 2009) and lack of connectivity with rivers (Gerke *et al.* 2010) make kettle ponds highly susceptible to external influence. Pond location in each given type of catchment yields an array of consequences associated with catchment functioning and the formation of a specific geo-ecological state. Until recently, the most common view was that kettle ponds and their catchments form outflow-free areas, which are not linked with the main hydrographic system. In effect, kettle ponds may serve as “traps” for pollution moving across a catchment (Waldon 2012). Their quality is also influenced by urbanisation, poor agricultural practices and untreated and industrial effluent (Burger *et al.* 2019).

Tiner (2003) argues that kettle ponds and their catchments form isolated areas in geographic space. At the same time, natural and anthropogenic changes may cause kettle ponds to link with any other hydrographic entities in their vicinity to form a complete hydrographic network (Chang *et al.* 2017). Recent research has shown that this may not always be the case. Kettle ponds may periodically change from outflow-free bodies to outflow-type bodies, which leads to changes in the circulation of water as well as changes in the catchment water supply and changes in water chemistry to flushing of pollutants stored in kettle ponds. Kalettka & Rudat (2006) have shown that some moraine kettle ponds in north-eastern Germany tend to overflow at high water stages, which connects them with the main hydrographic system in the catchment. This is important from the hydrological point of view of the basin. Water and mass exchange between rivers and lakes (kettle ponds) are key processes that maintain the health of the ecology of river–lake systems. Alteration to river–lake interactions has great impacts on water and mass balances (Yang *et al.* 2016).

While many different factors may affect pond water quality on a seasonal basis, major changes are generated by morphometry, catchment process dynamics, water supply pathways (Lischeid, Kalettka 2012), as well as human impact, especially in the form of intensifying agriculture (Koua *et al.* 2014), hydrotechnical construction (Praise *et al.* 2018), and increased atmospheric pollution, which is accompanied by atmospheric precipitation (Roba *et al.* 2014). Also, climate change adversely affects water quality (Johnson, Poiani 2016).

Recharge levels change during certain periods of the year due to changes in water levels in the catchment (Golus, Bajkiewicz-Grabowska 2016; Pietruszyński,

Cieśliński 2018). Hence, pond water quality does depend primarily on the sources of water supply. According to Lischeid and Kalettka (2012), who investigated basins without outlets in northern Germany, the above factors produce 90% of variation in pond water chemistry. Other factors include land use, agriculture-based pollution, primary production, and soil cover type. What is important is that kettle ponds are highly vulnerable to selected external factors due to their morphometry and hydrology (Gałczyńska, Gamrat 2007). According to Turner and Townley (2006) and Kacimov (2007) lakes and kettle ponds in lowland areas are hydraulically connected to a shallow groundwater system. In effect, pond water chemistry should be reflective of rainwater chemistry or groundwater chemistry.

The aim of the work is to determine the seasonal variability in the size of dissolved matter supplied to selected kettle ponds located in the glacial areas of northern Poland, using selected physicochemical indicators.

METHODS AND STUDY AREA

The main research effort focused on fieldwork including water sampling and related laboratory analysis as well as a review of source materials. The study area consisted of the drainage basin of the Parsęta River and a small catchment of the Borucinka River that flows across the Kaszubskie Lake District in northern Poland.

The Parsęta catchment (Figs 1, 2) is situated in Central Pomerania and occupies 3,150.9 km², or 1% of Poland’s area.

On the basis of detailed cartographic analyses (topographic maps at a scale of 1:10,000 – sheets in analogous and digital versions) and a field survey, six drainage basins of closed evapotranspiration basins were selected for stationary studies: Przeradz, Sławno, Kągle, Sadkowo, Gruszewo, and Rogowo, in the bottoms of which permanent or seasonal kettle ponds were found. All of them lie in the middle of fields (Table 1). Individual measuring sites were given names deriving from the nearby localities.

Three research sites (Przeradz, Sławno, and Kągle) were located in a lakeland elevation zone characterised by a great variety of landforms. The three remaining sites (Sadkowo, Gruszewo, and Rogowo) were situated within the borders of the 6th, 5th and 4th plateau levels, respectively.

The lakeland elevation subsides towards the north in the direction of the Baltic with a series of seven distinct, moraine plateau levels constituting the belt of coastal lowlands. Plateau levels are most often separated with clear morphological thresholds and are contained within specific height ranges. They exist in the form of numerous pieces separated with a rich system of mar-

ginal tunnels. This is the so-called North Pomeranian marginal zone saturated with a large number of kame forms correlated with kettle ponds (Karczewski 1988). The particular levels differ considerably in lithofacial variation which influences water cycle variation in the studied catchments of basins without outlets.

Atmospheric precipitation across open spaces was collected by an automated collector of wet precipitation manufactured by Eigenbrodt. Both pH and electrolytic conductivity were measured in samples collected daily via a total precipitation collector featuring a large intake surface area. The collector was exposed to precipitation all day long at the Geoecological Station operated by Adam Mickiewicz University in Storkowo – 4.5 km from the Przeradz research site.

Water samples were collected four times per year from the examined kettle ponds in each of four seasons of the year. Six piezometers were used to measure groundwater levels at the Przeradz research site. The devices were installed along the east-west line. Two piezometers were installed in depressions on the eastern and western sides of a pond (P1 and P2). P3 and P4 piezometers were installed halfway down a slope. Two piezometers were installed atop hill slopes along a water divide (P5, P6). One piezometer was installed in the Kragle catchment. In other catchments, groundwater samples were collected using two piezometers located on the opposite sides of

kettle ponds. The study period for the Parsęta drainage basin described in this paper consists of the hydrological years 2009–2010.

Research work in the Borucinka catchment began in November 2012 and was done by October 2014. Ten depressions (kettle ponds) were identified in this catchment (Fig. 3). Most of the kettle ponds are located in the western part of the catchment. This area is characterized by frequent changes in hydrographic structure as well as a seasonal hydrographic network that links kettle ponds together. This distribution of kettle ponds made it possible to determine the effect of changing water balance patterns on pond water quality. In addition, the kettle ponds examined were selected with differences in land use in mind, which made it possible to determine the effect of land use on pond water quality. Three types of land use were examined – agricultural, woodland, as well as farm-adjacent (Table 1).

In terms of land use, agricultural use of land prevails in the studied catchments, with arable land dominating. Despite the predominance of this form of land use in all the investigated drainage basins, only some of them were classified as agricultural catchments. The share of forests is relatively small, although these basins which were surrounded by quite large tree communities occupying over 30% of the catchment area and being a kind of protective barrier against pollution runoff, were classified as forest

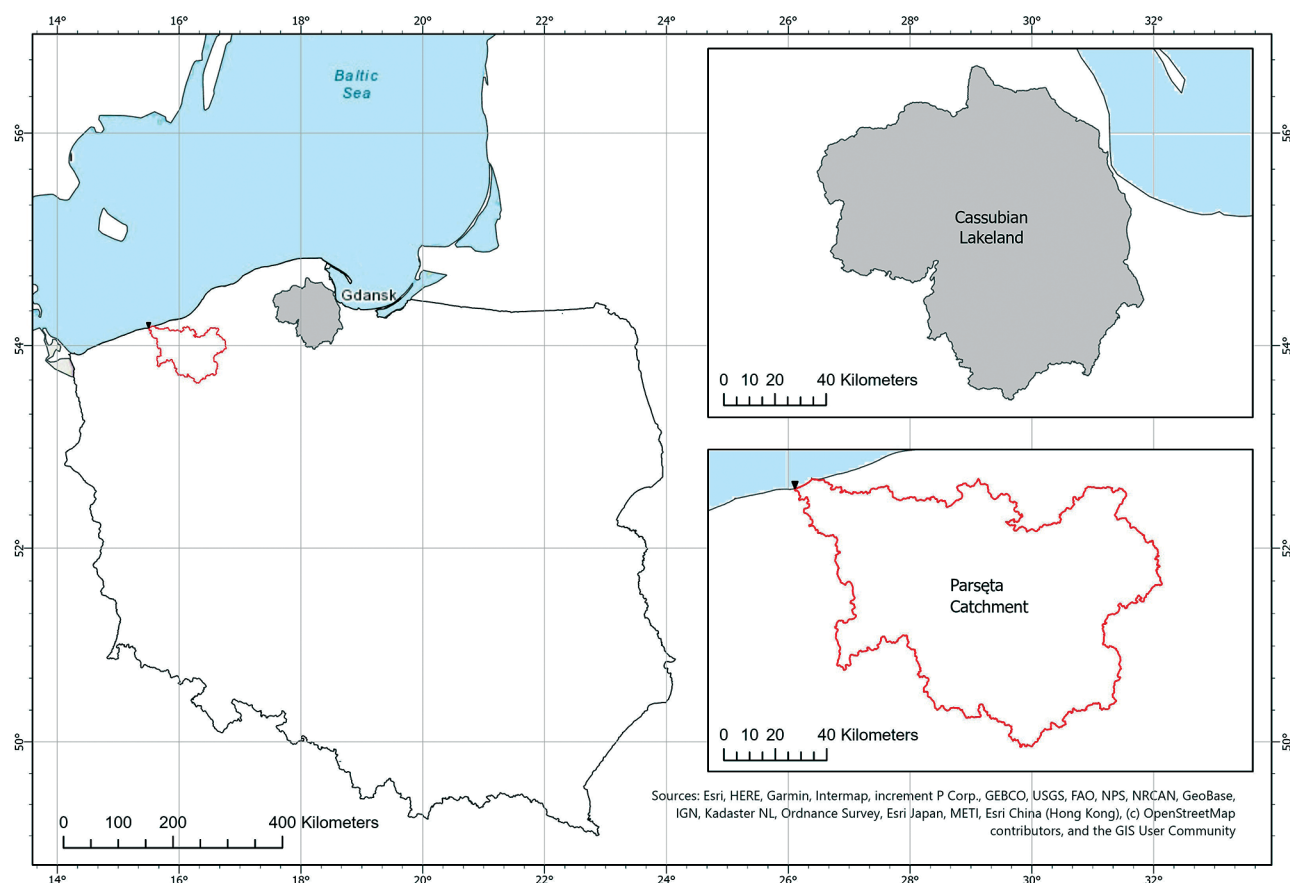


Fig. 1 Location of the Parsęta River basin and the Kaszubskie Lake District as compared with Poland

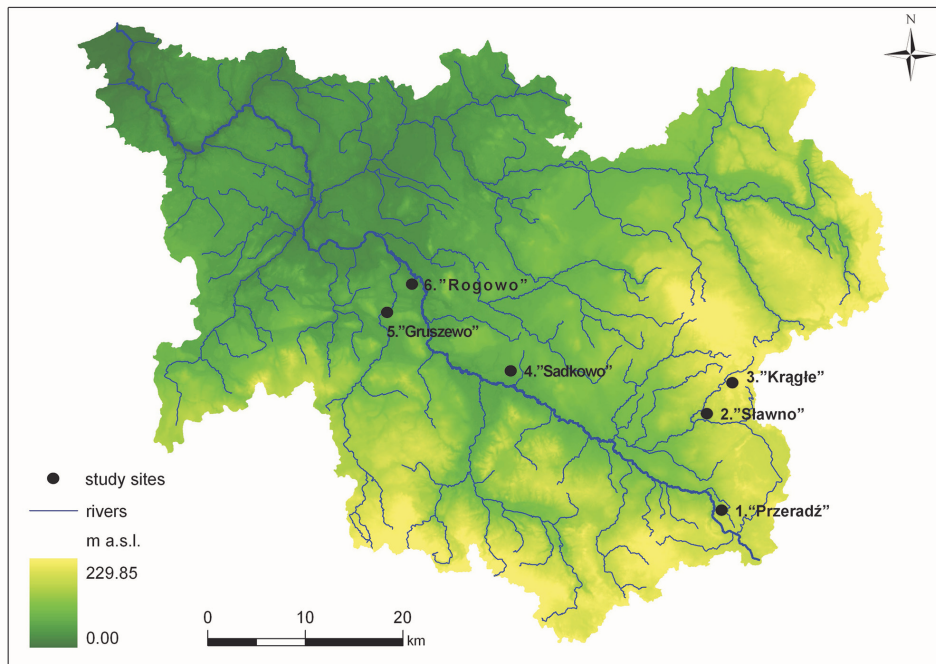


Fig. 2 Distribution of the closed basins under study in the Parsęta catchment

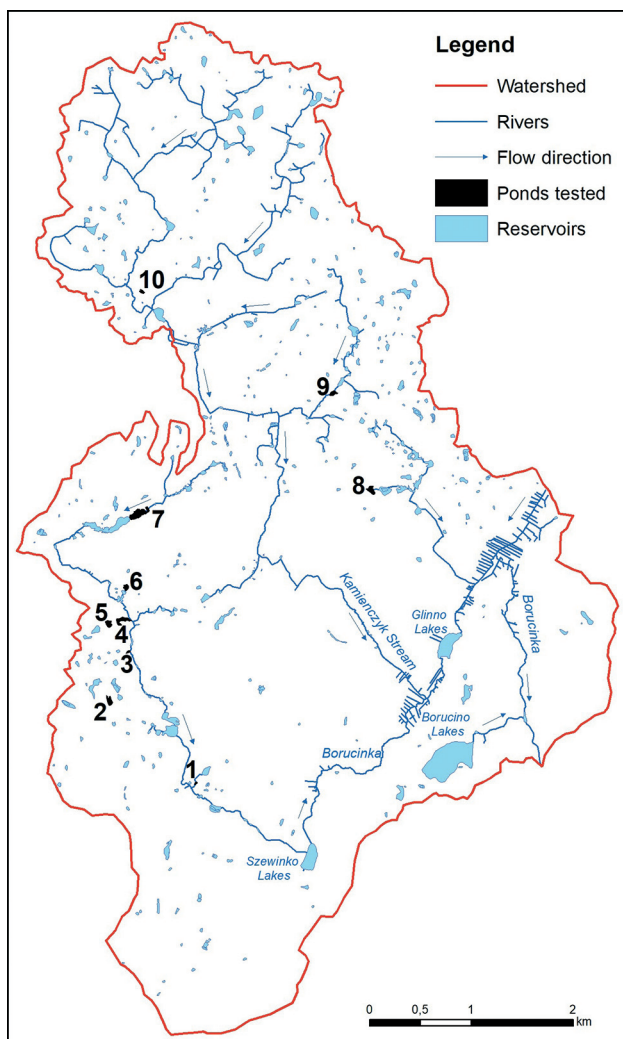


Fig. 3 Location of studied kettle ponds in the Borucinka catchment in the Kaszubskie Lake District

catchments. The catchments of kettle ponds situated in the immediate vicinity of farms with housing developments, which can significantly affect the delivery of pollution to the basin, were classified as farm-adjacent catchments.

Several key parameters were measured for each pond studied using a multi-parameter measurement device manufactured by HACH (models HQ30D and HQ40D): pH, electrolytic conductivity, oxygen content, and water temperature.

In the field, water samples were collected in chemically inert plastic containers. After the collection, the samples were stored in laboratory refrigerators at 4 °C. Hydrochemical analyses of the water samples taken in the Parsęta catchment were performed in the Analytical Laboratory of the AMU Geocological Station at Storkowo, using, among others, a Dionex DX-120 ion chromatograph and a Varian SpectrAA 20 Plus atomic absorption spectrometer; and those taken in the Borucinka drainage basin, in the Hydrochemical Laboratory of the Chair of Hydrology of Gdańsk University. They included the determination of the concentrations of basic cations and anions, as well as nitrates, phosphates and ammonia, using a Dionex ICS-1100 ionic chromatograph. The hydrogeochemical types of water were established using Shchukarijev's method. The types of water were distinguished on the basis of the content of seven basic ions: Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , and Cl^- , as well as three additional ones: NH_4^+ , NO_3^- , and PO_4^{3-} , if their levels in water exceeded 20% meq [mval] of the total of anions or cations (Beckett 2013). In order to determine the concentration of ions, the following

Table 1 Land use of the studied catchments of basins without outlets

Research area	Site	Land use (zone)	
Parsęta River basin	Przeradz	mid-field	lakeland elevation zone
	Slawno	mid-field	lakeland elevation zone
	Kragle	mid-field	lakeland elevation zone
	Sadkowo	mid-field	6th plateau level
	Gruszewo	mid-field	5th plateau level
	Rogowo	mid-field	4th plateau level
Borucinka catchment	1	farm-adjacent	4th plateau level
	2	agricultural	4th plateau level
	3	farm-adjacent	4th plateau level
	4	agricultural	4th plateau level
	5	woodland	4th plateau level
	6	woodland	4th plateau level
	7	agricultural	4th plateau level
	8	agricultural	4th plateau level
	9	farm-adjacent	4th plateau level
	10	agricultural	4th plateau level

analytical methods were applied: titration – acid-base titration (HCO_3^-) and complexometric edetate (Ca^{2+}), a spectrophotometer method – molybdate with stannous chloride (PO_4^{3-}) and with the Nessler reagent (NH_4^+), and an instrumental one – ion chromatography (SO_4^{2-} , NO_3^- , Cl^-), atomic emission spectrometry (Na^+ , K^+) and atomic absorption spectrometry (Mg^{2+}). To determine the concentration of ions with titration and spectrophotometer methods, use was made of reagent-grade chemicals. For chromatographs, a Dionex five anion standard concentrate was used to calibrate the instruments, and models were made by diluting it with deionized water. For spectrometer determinations, the Merck models were used for calibration. The quality control of the results concerned the comparison of the electrolytic conductivity measured and calculated and the calculation of an ion balance (the scope of the measurement error for the tested samples of surface waters in both catchments did not exceed 5%).

In the work, statistical analyses were carried out to determine the influence of geographical and anthropogenic determinants on the water quality in the investigated kettle ponds. To this end, use was made of multivariate analysis methods; the algorithm of the analytic procedure had two parts. In the first phase, diagnostic variables were reduced to a common comparative benchmark. Two procedures were used for this purpose: standardisation and bringing all the variables to destimulants. The second phase involved using the appropriate methods of multivariate analysis. In effect, the results for Perkal's synthetic indicator were compared with the multi-feature classification (by Ward's method with the Euclidean distance). These two methods were applied jointly to obtain an orderly picture of the water quality of the examined kettle ponds.

RESULTS AND DISCUSSION

Data for the Parsęta drainage basin were compared using various configurations with respect to time and geographic space in order to identify factors that affect seasonal changes in the supply of dissolved matter in the studied catchments. The data set is quite extensive due to its collection over many measurement cycles. The study is based on a comparison of the main parameters for two hydrological years (2009 and 2010) in order to capture changes occurring in different stages of water circulation. The first comparison focused on quarterly data for every season examined and included atmospheric precipitation measured across open spaces, as well as surface waters and groundwater in six monitored catchments. The second comparison was focused on monthly precipitation data and groundwater chemistry determined for piezometers P1 through P4, installed in the Przeradz catchment in the south-eastern section of the drainage basin of the Parsęta River.

The magnitude of the supply of dissolved matter to the examined catchments featuring kettle ponds is characterized by substantial variances over time. In many cases, trend lines are seen to follow a chaotic pattern. However, regardless of their shape, it is possible to observe a few seasonal patterns. Incomplete data for some study sites, as shown in the figures presented, are due to a lack of water in the studied basins without outlets at the time of measurement.

For 2010, all water types studied were characterized by a higher pH compared with that for 2009 due to a permanent tendency for pH to increase for precipitation waters in the recent 10 to 15 years. This increase results from improvements in air quality across Poland in the last couple of decades. The increasing pH of atmospheric precipitation is reflected in subsequent stages of water circulation or on the surface and underground. Regardless of the stable multi-annual trend, increasing pH was observed at each measurement site in the vegetation season of each hydrologic year, while pH decreases were observed in the winter season (Fig. 4a). The higher pH noted in the summer season for various water types was due to the leaching of the various chemical components of plant surfaces. This resulted in a reduction in its aggressiveness. On the other hand, the very low pH noted in the winter season was due to the burning of fossil fuels and the resulting emission of pollutants into the atmosphere leading to a decrease in pH at the various stages of water circulation.

The electrolytic conductivity of water depends first and foremost on the amount of the various salts dissolved therein (Table 2, Fig. 4b). Hydrometeorologic conditions in the area of interest are also quite relevant, especially air temperature and the atmospheric precip-

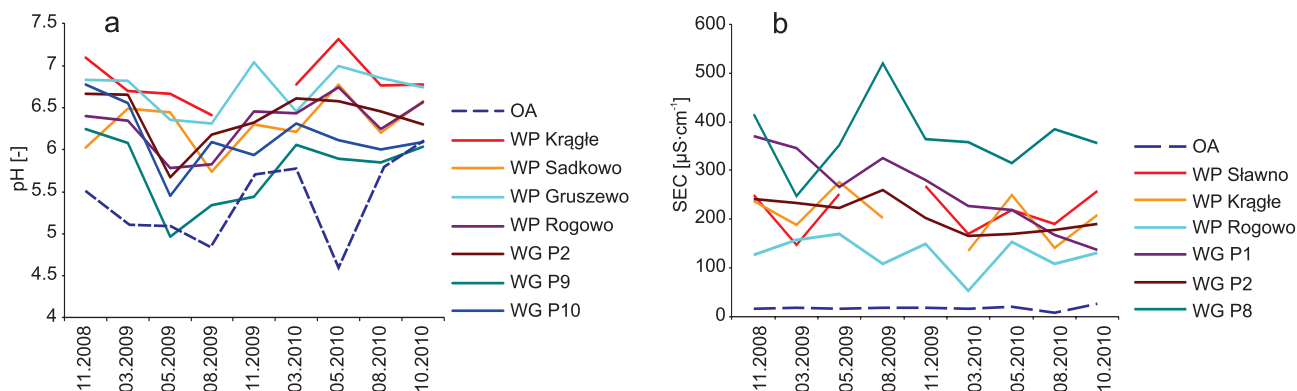


Fig. 4 Seasonal variances in pH (a) and electrical conductivity (SEC) (b) in the examined catchments of basins without outlets in the Parsęta drainage basin in the hydrological years 2009–2010. OA – atmospheric precipitation across open spaces at the Geocological Station in Storkowo, WP – surface waters, WG – groundwater

Table 2 Examples of the mean values of the analysed physiochemical parameters of surface waters in the examined kettle ponds in the Parsęta River basin in the hydrological years 2009–2010

Site	pH	SEC	HCO ₃ ⁻	PO ₄ ³⁻	Ca ²⁺	Mg ²⁺	K ⁺	NH ₄ ⁺
	[-]	[µS·cm ⁻¹]	[mg·dm ⁻³]					
Przeradz	5.41	142.07	20.24	0.30	13.52	0.78	1.44	1.03
Sławno	6.43	218.83	112.81	1.24	35.47	3.28	4.55	1.19
Krażle	6.81	204.36	122.35	1.08	39.07	1.72	2.98	0.59
Sadkowo	6.31	122.78	55.39	0.19	16.67	3.37	3.71	0.90
Gruszewo	6.71	92.47	49.02	0.06	11.56	2.19	4.05	0.74
Rogowo	6.31	128.02	61.70	0.54	13.01	2.40	9.50	1.26

itation total (Table 3). The latter is a key determinant of the amount of wet deposition reaching the parent material (Morison et al. 2017). The hydrological year 2009 in the Parsęta River basin was normal in terms of the annual amount of precipitation with its total of 748 mm, and the year 2010 was humid with the annual precipitation total of 784.8 mm. In Poland, rainfall in a summer half-year prevails with its relation being very similar from about 60 to 40%. This was confirmed by the research on seven Base Stations of the Integrated Monitoring of the Natural Environment in Poland in the hydrological years of 2006–2007 (Major 2007, 2008). In the summer measurement period, rainfall conditions varied. There were permanent rain-free periods at that time, especially at the end of summer, in August, September and October. In turn, in the Borucinka catchment the year 2013 was normal, whereas 2014 was dry. In the hydrological year 2013, the total monthly precipitation fluctuated between 17.4 mm in March and 84.2 mm in November. In the hydrological year 2014, the highest monthly precipitation total was recorded in May (82.3 mm), whereas the lowest in February (11.4 mm). In the analysed years, relatively low rainfall was also noted in April (28.7 and 26.7 mm, respectively).

Rain storms and torrential rains are of particular importance for the functioning of streams and basins in the Borucinka catchment due to the delivery of a considerable amount of water. In the hydrological

Table 3 Annual precipitation totals [mm] in the hydrological years 2009–2010 in the Parsęta River basin and in the Borucinka catchment

Hydrological year	Parsęta River basin	Borucinka catchment
2009	748.0	615.0
2010	784.8	598.2

year 2013, the number of days with the precipitation ≥ 10 mm was 17 with only one day with the precipitation ≥ 20 mm (29 November 2012–22.3 mm). In the hydrological year 2014, fewer days with the precipitation ≥ 10 mm (12 days) were observed with four days with the rainfall ≥ 20 mm. This amount of precipitation is rare and is most often noted in a warm half-year. The highest precipitation total in the hydrological year 2014 was recorded on 24 May 2014 and it was 45.6 mm. The measurement in the examined catchment was carried out two days after this rainfall.

Bicarbonate and calcium ions are the predominant components of the examined waters that determine the hydrogeochemical water type and help increase conductivity (Tables 4, 5). Similar statistic comparisons were made for all the analysed components. The main source of both ions is the process of chemical weathering, and their quantity increases with increasing depth of the surface of the groundwater aquifer. In the context of the above, a correlation is observed in this case, where the three examined parameters (electrical conductivity and concentrations of HCO₃⁻ and

Ca²⁺) vary almost identically from season to season (Fig. 5a). Concentrations of magnesium also followed a similar seasonal pattern. The source of magnesium is similar to the source of bicarbonate and calcium – the leaching of rocks and soils as well as the process of chemical weathering (Fig. 5b).

The next trend concerns ammonium and phosphate ions whose concentrations follow a pattern of large fluctuations from season to season. Both ions are considered to be biogenic components of the natural environment that help accelerate the eutrophication of water. Their concentrations tend to be small relative to those of other chemical components of the natural environment, but in the examined catchments of basins without outlets the concentrations of these ions were high enough to affect several classes of water quality. These concentrations were high to the point of meaningfully worsening surface and groundwater quality across the study area. The most often observed seasonal change in biogenic substance concentration is a large increase in the winter season due to the process of leaching from the soil. Conversely, in summer, the concentration of biogenic substances decreases due

to their uptake by living organisms (biological absorption), which leads to a relative increase in the concentration of all other components of the soil or water. This pattern may become disrupted by the supply of any household wastewater or water from agricultural areas arriving in the area of interest.

A similar pattern was observed in the course of each studied hydrologic year in water samples obtained from the examined catchments with basins without outlets. Lower NH₄⁺ and PO₄³⁻ concentrations were observed in summer when plants absorb these ions during periods of higher temperature and ammonium ions experience nitrification. In August, the highest concentrations of ammonium and phosphate were noted, as the vegetation season is nearing its end (Fig. 6) and these ions are no longer used in the plant growth process; they instead become available in the aeration layer. Research has shown that air temperatures are no longer the highest at this time and the rate of nitrification is also below its peak value.

The supply of dissolved matter to the Borucinka catchment followed a pattern similar to that for the Parsęta drainage basin – significant variances over

Table 4 Basic statistics for bicarbonate ions [mg·dm⁻³] in the examined kettle ponds in the Parsęta River basin

Site	Mean	Median	Minimum	Maximum	25,000 percentile	75,000 percentile	Standard deviation
Przeradz	16.97	17.39	6.10	32.34	9.76	22.88	7.84
Sławno	112.81	115.33	57.97	165.36	81.77	142.48	37.22
Kraśle	122.35	112.58	86.04	185.50	94.28	146.75	34.95
Sadkowo	55.39	53.09	20.75	89.09	43.93	64.68	20.55
Gruszewo	49.02	48.82	33.56	63.46	42.71	52.48	9.40
Rogowo	61.70	65.90	33.56	78.11	59.80	73.22	15.54

Table 5 Basic statistics for calcium [mg·dm⁻³] in the examined kettle ponds in the Parsęta River basin

Site	Mean	Median	Minimum	Maximum	25,000 percentile	75,000 percentile	Standard deviation
Przeradz	15.59	12.71	9.46	32.14	10.26	17.11	7.58
Sławno	35.47	36.55	20.76	46.65	30.38	41.24	8.21
Kraśle	39.07	38.44	23.73	59.16	31.30	45.09	11.13
Sadkowo	16.67	16.51	5.13	25.33	13.79	20.12	5.93
Gruszewo	11.56	12.50	8.50	14.03	9.78	13.31	2.19
Rogowo	13.01	13.23	4.73	19.08	11.06	15.31	4.38

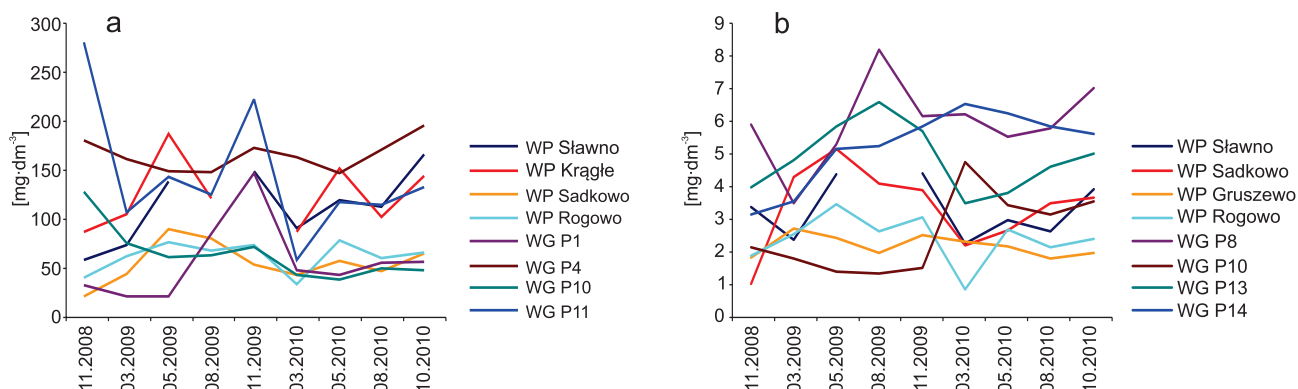


Fig. 5 Seasonal variances in bicarbonate ions (HCO₃⁻) (a) and magnesium (Mg²⁺) (b) in the examined catchments of basins without outlets in the Parsęta drainage basin in the hydrological years 2009–2010. WP – surface waters, WG – groundwater

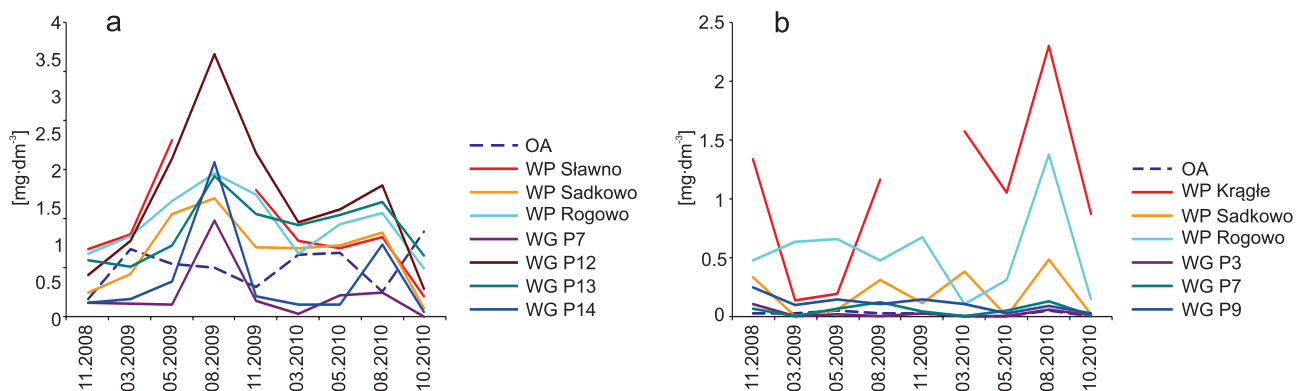


Fig. 6 Seasonal variances in ammonium (NH_4^+) (a) and phosphates (PO_4^{3-}) (b) in the examined catchments of basins without outlets in the Parsęta drainage basin in the hydrological years 2009–2010. OA – atmospheric precipitation across open spaces at the Geocological Station in Storkowo, WP – surface waters, WG – groundwater

time, with trend lines that do appear quite chaotic at times. The lack of data for some points results from a lack of water in basins without outlets at the time of measurement or due to surface ice. The next section provides a brief characterization of changes over time and geographic space with respect to selected physical and chemical indices.

The pH of water in the studied kettle ponds was close to neutral throughout the study period. The fluctuation range in pH varied from 5.8 (pond 3) to 8.9 (pond 2). No permanent trend in pH values was noted over the studied period of time. However, pH values did vary by a substantial amount over time. Pond 3 was characterized by the most stable pH range at 0.8 pH units. The largest fluctuations in water pH were noted in pond 7 (change range of 2.7 pH units). Slightly basic waters were noted in summer, while slightly acidic waters in spring and winter.

The electrical conductivity of the tested water samples was quite stable and small. The only kettle ponds to deviate from “normal” values obtained for most kettle ponds were pond 1 and also pond 3 (early measurement dates). The highest value ($224 \mu\text{S}\cdot\text{cm}^{-1}$) was obtained for pond 1, while the lowest value ($23.4 \mu\text{S}\cdot\text{cm}^{-1}$) was obtained for pond 2. Conductivity values were most stable during the study period for pond 4, with a fluctuation range from 35.8 to $41.1 \mu\text{S}\cdot\text{cm}^{-1}$. Other kettle ponds were characterized by low electrical conductivity values, which is a signal that atmospheric precipitation plays a dominant role. Elevated electrical conductivity values were noted only during the winter season and in the course of spring snowmelt season.

Bicarbonate concentrations were quite random, although the range for most kettle ponds was 20 to $40 \text{ mg}\cdot\text{dm}^{-3}$. Only the concentration for pond 1 was markedly higher than those for all other studied kettle ponds, ranging from 36.6 to $128.1 \text{ mg}\cdot\text{dm}^{-3}$. All other kettle ponds ranged from 6.1 to $61.0 \text{ mg}\cdot\text{dm}^{-3}$. This illustrates large bicarbonate differences between the studied kettle ponds. The largest fluctuations in the

bicarbonate range were noted for kettle ponds 1, 3, and 9. At the same time, it may be noted that HCO_3^- is a dominant ion in the studied kettle ponds wielding significant influence over their hydrogeochemical water type.

There does not exist a stable pattern of change for the chloride ion with respect to time for the studied kettle ponds. The only observed pattern is that of increasing chloride concentration in periods following heavy rainfall events, which suggests that atmospheric precipitation plays a major role. The chloride concentration range was found to be from $1.3 \text{ mg}\cdot\text{dm}^{-3}$ in pond 2 to $11.2 \text{ mg}\cdot\text{dm}^{-3}$ in pond 9. These values show that the studied kettle ponds are often strongly dominated by freshwater, with stable chloride content, while most water is obtained from atmospheric precipitation. The change range is very small for most of the studied kettle ponds, on the order of several milligrams throughout the entire study period.

The sulfate concentrations in the studied pond water in the Borucinka catchment were small. The distribution of fluctuations resembles (to some extent) that observed for electrical conductivity – ranging from 0.1 to $16.1 \text{ mg}\cdot\text{dm}^{-3}$ for all the kettle ponds studied. A comparison of minimum and maximum values obtained for the study period indicates that pond 1 differs substantially from all other kettle ponds studied. The range of sulfate values starts at $2.9 \text{ mg}\cdot\text{dm}^{-3}$ and reaches a value of $16.1 \text{ mg}\cdot\text{dm}^{-3}$. As in the case of chloride concentrations, the highest sulfate concentrations in the water of the studied kettle ponds were noted following heavy rainfall, which may suggest that this ion arrives via pollution reaching the catchment through precipitation. On the other hand, the lowest sulfate concentrations were noted in summer. It may be argued that sulfate concentrations follow a distribution similar to that of SEC, and this means that sulfate strongly affects the hydrogeochemical water type of kettle ponds. In addition, sulfate ions may reach kettle ponds as a result of throughflow from hill slopes

surrounding the kettle ponds. The primary sources of sulfate in the soil profile are chemical weathering and decomposition of organic matter (Szpikowski *et al.* 1998). Multiple-cycle leaching leads to an increase in mineralization and transformation of the geochemical type (Limantseva *et al.* 2016).

The concentration of Ca^{2+} in the examined kettle ponds in the Borucinka catchment ranged from $2.0 \text{ mg}\cdot\text{dm}^{-3}$ (pond 2) to $39.4 \text{ mg}\cdot\text{dm}^{-3}$ (pond 1). Pond 1 is characterized by exceptionally large fluctuations in the concentration of calcium in the study period relative to all the other studied kettle ponds. Its content ranged from 12.0 to $39.4 \text{ mg}\cdot\text{dm}^{-3}$. The Ca^{2+} content in all the other examined kettle ponds was found to be stable, although there exists a lack of similar patterns. The calcium ion “dominates” the examined waters and significantly affects the hydrogeochemical water type of the studied kettle ponds.

In summary, the main source of bicarbonate ions and calcium ions in this study is the process of chemical weathering. In this context, there exists a relationship, as in the case of the Parsęta drainage basin, whereby three parameters follow a very similar seasonal pattern – this applies to electrolytic conductivity and the concentrations of HCO_3^- and Ca^{2+} .

The range of sodium ion concentrations in the kettle ponds of the Borucinka catchment was found to be small. There is also a lack of stable and similar change tendencies for each given pond. The studied kettle ponds are characterized by similar sodium ion concentrations and marginal changes therein during the study period. Sodium content ranged from $0.76 \text{ mg}\cdot\text{dm}^{-3}$ in pond 6 to $4.24 \text{ mg}\cdot\text{dm}^{-3}$ in pond 9.

The study of kettle ponds in the Borucinka catchment showed a pattern of higher potassium concentrations versus sodium concentrations, as applicable to pond 3 (Fig. 7). This pond featured the highest concentration ranges for potassium, which provided for a stark contrast with other kettle ponds in the study sample (from 3.4 to $34.7 \text{ mg}\cdot\text{dm}^{-3}$). This high concentration does suggest that pond 3 is polluted with potassium salts. High mean K^+ concentrations were also noted for pond 1 (from 3.7 to $13.7 \text{ mg}\cdot\text{dm}^{-3}$) (Fig. 7). All the remaining kettle ponds were found to feature low potassium ion concentrations ranging from 0.7 to $6.7 \text{ mg}\cdot\text{dm}^{-3}$. The K^+ content of these kettle ponds did not vary substantially over the course of the study period (Fig. 7). Research in the Parsęta drainage basin has shown a dual tendency of higher potassium ranges versus sodium ranges in five surveyed kettle ponds. A similar situation was observed in the Gniezno Lake District in central Poland, where the mean potassium ion concentration in surface waters stood at $30.1 \text{ mg}\cdot\text{dm}^{-3}$. This was more than three times the concentration value of the mean value for the sodium ion, which stood at $8.9 \text{ mg}\cdot\text{dm}^{-3}$. This high

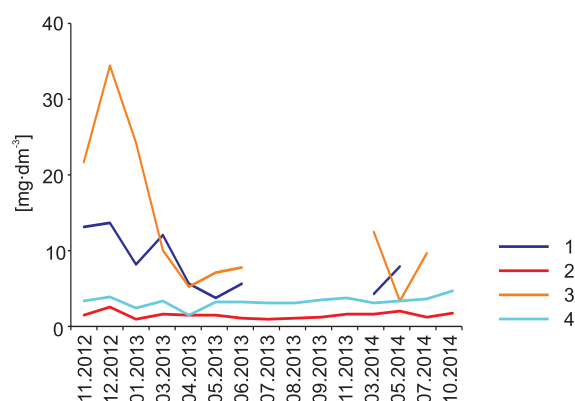


Fig. 7 Changes in water potassium (K^+) over time in selected kettle ponds in the Borucinka River catchment. 1, 2, 3, 4 – numbers of selected kettle ponds

concentration of potassium in pond water cannot be easily explained by natural processes, as it may be the result of improper fertilization using potassium fertilizers or some other form of human impact.

Magnesium ion concentrations in the studied kettle ponds in the Borucinka catchment were low – ranging from $0.01 \text{ mg}\cdot\text{dm}^{-3}$ in pond 3 to $2.2 \text{ mg}\cdot\text{dm}^{-3}$ in pond 1. The magnesium concentration range was small for the given group of kettle ponds over the study period. It suggested two main sources of recharge – atmospheric precipitation and groundwater supply associated with the leaching of rocks.

The nitrate concentration in the water of the studied kettle ponds was rather small – ranging from $0.00 \text{ mg}\cdot\text{dm}^{-3}$ for all the studied kettle ponds to $2.17 \text{ mg}\cdot\text{dm}^{-3}$ in pond 3 (Fig. 8a). A large increase in the concentration of nitrate was observed on 25 May 2014 following heavy rainfall (Fig. 8a). As a result, the nitrate concentration increased about threefold in May 2014. This type of increase in the concentration of nutrients following rainfall is natural. Nitrate reaches bodies of water mainly via atmospheric precipitation and surface runoff. The highest nitrate concentrations for kettle ponds 1, 3, and 6 relative to the entire study period were noted in May 2014: $0.34 \text{ mg}\cdot\text{dm}^{-3}$ in pond 1, $1.92 \text{ mg}\cdot\text{dm}^{-3}$ in pond 6, and $2.17 \text{ mg}\cdot\text{dm}^{-3}$ in pond 3 (Fig. 8a).

The concentration of the ammonium ion was very low for most of the year in all of the examined kettle ponds – below the level of detection. A marked increase in ammonium content was detected only after heavy rainfall in May 2012 for pond 1 and in December 2012 for pond 3. The ammonium concentration range was 0.00 to $1.88 \text{ mg}\cdot\text{dm}^{-3}$.

The concentration range for phosphate was small for the studied kettle ponds. Only pond 3 experienced some meaningful variance (Fig. 8b). Kettle ponds 1 and 5 also experienced minor variance (Fig. 8b). For pond 3, the phosphate concentration range was 0.00 to $3.69 \text{ mg}\cdot\text{dm}^{-3}$. Elevated values were noted for pond 3 in December 2012 and January 2013. Elevated val-

ues were noted for kettle ponds 1 and 5 in May 2014 (Fig. 8b): 1.94 mg·dm⁻³ and 1.71 mg·dm⁻³, respectively. The high phosphate concentration during the periods given above was most likely associated with the leaching of potassium compounds from sediments and soils in the course of intense atmospheric precipitation and snowmelt events.

Given the large differences in physical and chemical data for pond 1 relative to all the other studied kettle ponds, it was decided to attempt to explain the reasons for this difference. In summary – pond 1 is located in an upland area at 205 meters above sea level and features a surface area of 0.05 hectares, while its catchment area is 5.9 hectares. The pond is located in the southern part of its small catchment, which includes homes and farm buildings (7% of the catchment area). Arable land covers 72% of the catchment area. The central part of the area is a wetland area, which recharges the examined pond at high water stages. Pond 1 is a flow-through pond at high water stages. At low water stages, it dries up.

Finally, examples of the mean values of the analysed physiochemical parameters were presented in tabular form (Table 6) and, as was in the case of the Parsęta catchment, basic statistics for bicarbonate ions (Table 7) and calcium (Table 8).

Additionally, Fig. 9 presents Perkal's synthetic indicator, which made it possible to arrange the analysed objects along a number line on the basis of the concentrations of the measured substances obtained in the examined kettle ponds. With regard to the synthetic indicator, the classification according to the Hellwig critical separation method was applied (in this case for $k = 0.5$). Weights of all variables were equal. Since the examined features are destimulants, higher values of the synthetic indicator correspond to a worse water quality of the examined kettle pond, whereas lower – to a better quality of water.

With the above synthetic indicator, four groups of kettle ponds were distinguished. The first included kettle pond 1 characterised by a very high value of the measured indicator (the worst quality of water). The second group consisted of objects with a high synthetic indicator (a low quality of water) with kettle ponds 3 and 9. The third covered kettle ponds with a mean value of the synthetic indicator (an average water quality) – kettle ponds 10 and 8. The last comprised objects with the lowest value of the measured indicator (kettle ponds 5, 7, 4, 6, 2 with the best water quality) (Fig. 10).

Fig. 10 presents the result of the multi-feature classification in the form of a dendrite. It results in the

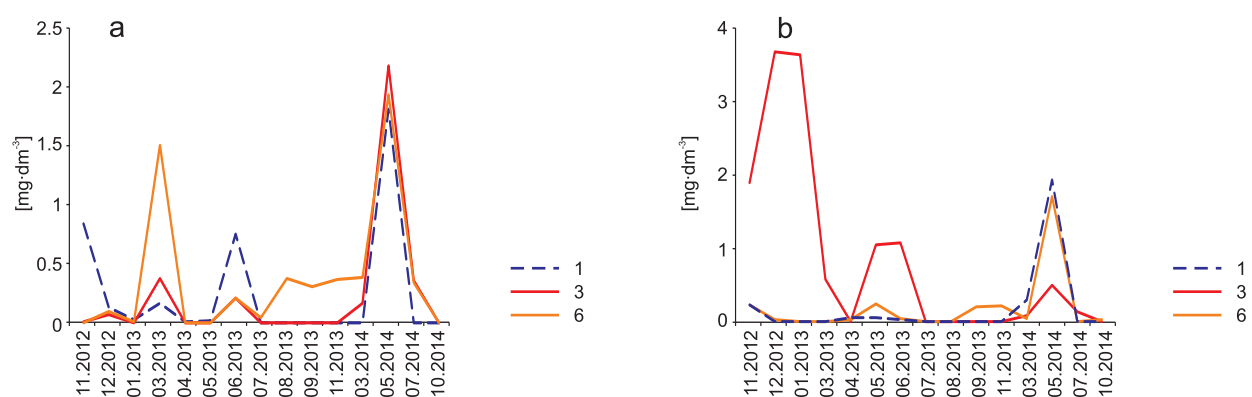


Fig. 8 Changes in water nitrates (NO_3^-) (a) and phosphates (PO_4^{3-}) (b) over time in selected kettle ponds in the Borucinka River catchment. 1, 3, 5, 6 – numbers of selected kettle ponds

Table 6 Examples of the mean values of the analysed physiochemical parameters of surface waters in the examined kettle ponds in the Borucinka River basin in the hydrological years 2013–2014

No. of kettle pond	pH	SEC	HCO_3^-	PO_4^{3-}	Ca^{2+}	Mg^{2+}	K^+	NH_4^+
	[-]	[$\mu\text{S}\cdot\text{cm}^{-1}$]	[$\text{mg}\cdot\text{dm}^{-3}$]					
1	7.38	153.8	86.44	0.288	28.09	1.52	8.28	0.317
2	7.04	23.4	11.80	0.223	2.97	0.67	1.46	0.094
3	6.27	74.9	33.86	1.266	4.94	0.88	13.68	0.306
4	7.11	38.1	19.93	0.076	4.98	0.69	3.26	0.059
5	7.00	36.6	19.61	0.196	4.90	0.94	3.10	0.096
6	6.50	35.7	16.68	0.076	5.04	0.78	1.63	0.035
7	7.00	28.4	12.20	0.086	3.46	0.69	1.60	0.035
8	7.10	68.0	38.44	0.045	11.82	1.22	2.55	0.012
9	6.93	65.6	27.86	0.152	8.40	1.30	5.12	0.104
10	6.58	50.2	21.82	0.178	6.90	1.25	2.76	0.117

Table 7 Basic statistics for bicarbonate ions [$\text{mg} \cdot \text{dm}^{-3}$] in the examined kettle ponds in the Borucinka River basin

No. of kettle pond	Mean	Median	Minimum	Maximum	25,000 percentile	75,000 percentile	Standard deviation
1	86.4	91.5	33.6	128.1	51.86	115.93	34.21
2	11.8	12.2	6.1	18.3	9.15	12.20	3.02
3	33.9	33.6	18.3	61.0	18.30	45.76	14.49
4	19.9	18.3	12.2	24.4	18.30	21.36	3.23
5	19.6	18.3	15.3	24.4	18.30	21.36	2.86
6	16.7	15.3	12.2	24.4	12.20	18.30	4.14
7	12.2	12.2	9.2	15.3	9.15	15.25	2.82
8	38.4	39.7	30.5	45.8	33.56	42.71	5.00
9	26.6	27.5	15.3	45.8	21.36	33.56	9.00
10	21.4	21.4	12.2	27.5	21.36	24.41	4.29

Table 8 Basic statistics for calcium [$\text{mg} \cdot \text{dm}^{-3}$] in the examined kettle ponds in the Borucinka River basin

No. of kettle pond	Mean	Median	Minimum	Maximum	25,000 percentile	75,000 percentile	Standard deviation
1	28.01	30.7	11.96	39.38	18.16	38.42	10.31
2	2.97	3.2	1.96	3.76	2.31	3.54	0.63
3	4.94	5.0	2.68	7.33	4.20	6.13	1.23
4	4.98	5.0	3.86	6.51	4.62	5.23	0.63
5	4.90	4.8	4.02	6.94	4.39	5.26	0.79
6	5.04	4.9	3.04	9.25	3.81	6.14	1.61
7	3.46	3.4	2.86	5.23	2.93	3.87	0.69
8	11.82	12.0	9.81	13.73	10.91	12.83	1.13
9	8.40	8.0	5.49	11.49	6.79	9.82	1.91
10	6.90	7.0	4.59	8.52	5.94	7.77	1.16

division of all the examined objects into two groups: A and B. The first (A) includes kettle ponds 8, 6, 5, 7, 4, 2. A distinguishing feature in this group is a low content of nitrogen and phosphorus compounds, as well as Cl^- and Na^+ . The second group (B) consists of kettle ponds 10, 9, 3, and 1, which are characterised by high nitrogen compound values, as well as Cl^- and Mg^{2+} (Fig. 10).

The comparison of the calculated Perkal's synthetic indicator with the result of the multi-feature classification is presented in Table 9. What can be observed is the relationship between the synthetic indicator and the applied multi-feature classification because A-type kettle ponds have low and average values of the indicator, whereas for kettle ponds from group B its values are high and very high.

One can observe a clear impact of land use on the concentration of the examined elements. Kettle ponds of type A with a low value of the synthetic indicator constitute the most numerous group and have the best water quality of all the investigated objects. This group consists of kettle ponds the catchments of which were classified as woodland (kettle ponds 5 and 6) (Table 9). Trees around kettle ponds are a green buffer zone separating them from agricultural land and farms. Ryszkowski and Kędziora (1987) as well as Karg *et al.* (2003) state that compact tree and shrub belts can mitigate the influence of external factors building the chemical properties of kettle ponds. Gałczyńska and Gamrat (2007) draw attention to the fact that the existence of trees around kettle ponds, es-

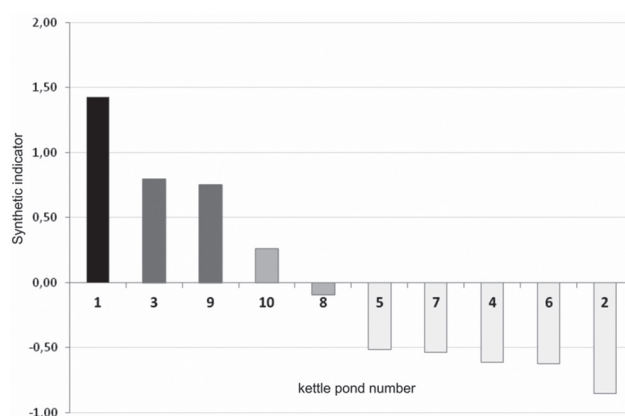
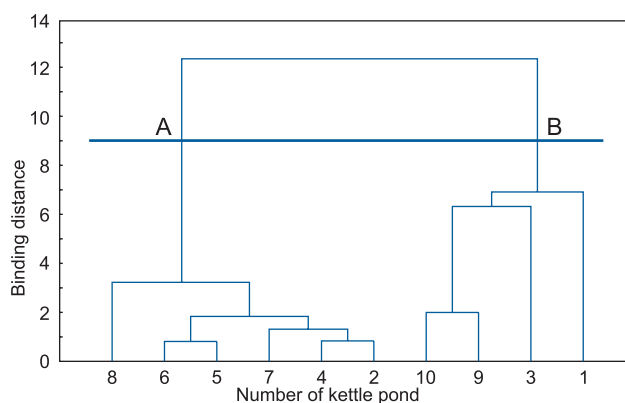
**Fig. 9** Arrangement of the examined kettle ponds in relation to the obtained concentrations of the investigated substances with Perkal's synthetic indicator**Fig. 10** Classification of the examined kettle ponds in the Borucinka catchment in terms of chemical composition according to the Ward method (the Euclidean distance)

Table 9 Comparison of Perkal's synthetic indicator and the multi-feature classification

Synthetic indicator of water quality	Type	
	A	B
low – best water quality	2, 6, 4, 7, 5	
average – average water quality	8	10
high – poor water quality		9, 3
very high – worst water quality		1

pecially in basins without plant life on the water surface, positively affects the concentration of biogenic substance and the reduction of water temperature.

B-type kettle ponds, which have a high and very high value of the synthetic indicator (kettle ponds 1, 3, and 9) (Table 9) are reservoirs adjacent to farms. Their water quality is the worst of all the examined objects. It may be indicative of a considerable influence of point-source pollution in forms of houses and farm buildings. These basins, which are exposed to a large impact of farms very often not connected to the sewage system, can collect farm-adjacent waste water (Williams *et al.* 2015). This is to a large extent agricultural waste coming from a manure pit stored in a farm.

The remaining basins were classified as agricultural (ponds 2, 4, 7, 8, 10) with a dominating type of land use in the form of farmland. No significant influence of farms and buffers of woodland was observed. Their synthetic indicator was average or low and they belonged to type A, except for kettle pond 10 which was part of type B (Table 9).

Kettle pond 7 with the largest area (0.96 ha) and capacity (8,582.8 m³) was also characterised by a low value of the measured synthetic indicator, i.e. the best water quality. The large area and capacity can affect the reduction and equalization of the amplitude of the concentration of the studied compounds (Cl⁻, HCO³⁻, K⁺, Mg²⁺, Ca²⁺) by diluting pollution flowing into its waters. Two basins without outlets were also included in the group of kettle ponds with a low value of the synthetic indicator (ponds 2 and 4).

To sum up, it can be stated that pond permanence in wetlands primarily is a function of the relation between evaporation and precipitation rates (Hayashi *et al.* 2016), and their relation to other water balance components, such as groundwater exchange, pond water levels, fluctuate seasonally and annually (van der Valk 2005). It can be clearly visible in the investigated areas, especially in the Borucinka catchment. Given that kettle ponds rarely make surface contact with the entire hydrographic network, their water quality depends primarily on vertical water exchange, and especially on atmospheric (Sobel *et al.* 2003). What was observed in the examined areas during many periods were concentrations of selected physiochemical indicators similar to those recorded in precipitation waters. Lischeid and Kalettka (2012) argue that pond

water retention times and water exchange pathways serve as the main determinants of the stability of water chemistry in kettle ponds, which is also observed in the studied areas. It concerns particularly periods of including ponds in the main hydrographic system. In effect, they can occur in equilibrium states of the geochemical system (Shvarov 1999). Other ideas are proposed by Golus and Bajkiewicz-Grabowska (2016) who argue that pond water quality is determined by water throughflow. In turn, Pietruszyński and Cieśliński (2018) found that the main reason for the higher concentration of selected ions in the kettle ponds is the proximity of farms producing sewage that reach water reservoirs in the studied area, as well as the hydrological function of the kettle ponds they perform (outflow – flow). This last statement is important because the research was also conducted in the Borucinka catchment. According to Yu *et al.* (2015), small shallow seasonal wetlands with a short hydroperiod play an important role in the entrapment of nutrients and, due to their wide distribution, in determining the water quality of watersheds.

CONCLUSIONS

On the basis of the obtained results, the following conclusions can be drawn:

1. Climate conditions served as the primary determinants of seasonal change in the supply of dissolved matter to basins without outlets in the Parsęta drainage basin during the study period. In turn, in the Borucinka catchment, the main determinant of the hydrochemical state of kettle ponds was land use. In addition, their hydrologic function may also affect their hydrochemistry over time.

2. The pH of water in the studied kettle ponds was close to neutral throughout the study period. The higher pH noted in the summer season for various water types was due to the leaching of the various chemical components of plant surfaces. On the other hand, the very low pH noted in the winter season was due to the burning of fossil fuels and the resulting emission of pollutants into the atmosphere leading to a decrease in pH at the various stages of water circulation.

3. The electrolytic conductivity of water depends first and foremost on the amount of the various salts dissolved therein. Hydrometeorologic conditions in the area of interest are also quite relevant, especially air temperature and the atmospheric precipitation total.

4. Seasonal changes of biogenic substances resulted from the length of the vegetation season.

5. Seasonal shifts in the concentration of selected ions were determined by the intensity of rock and soil leaching as well as the rates of chemical weathering.

6. Bicarbonate and calcium ions are the predomi-

nant components of the examined waters that determine the hydrogeochemical water.

7. Increasing chloride concentration in the periods following heavy rainfall events suggests that atmospheric precipitation plays a major role in the studied kettle ponds.

8. The highest sulfate concentrations in the water of the studied kettle ponds were noted following heavy rainfall, which may suggest that this ion arrives via pollution reaching the catchment through precipitation.

9. Concentrations of ammonium and phosphate ions are characterized by large fluctuations from season to season. The most often observed seasonal change in biogenic substance concentration is a large increase in the winter season due to the process of leaching from the soil. Conversely, in summer, the concentration of biogenic substances decreases due to their uptake by living organisms.

ACKNOWLEDGMENTS

The authors are grateful to two anonymous reviewers for valuable remarks and suggestions that allowed improving the manuscript.

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