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Hydrochemical aspects of water exchange through the bottom of headwater stream in suburban zone on the example of the Malina watercourse in Zgierz (Central Poland)

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Abstract: Among the many factors determining the quality of river waters, the influence of the hyporheic zone (HZ) is gaining in importance. Watercourses that exist in the higher parts of catchments are relatively steep and shallow, and the topography of their valleys activate hyporheic flow. The main goal of this work is to assess the impact of the HZ on the hydrochemical state of the head watercourse of the Malina in the suburbs of the city of Zgierz with the focus on biogenic compounds. The riverbed of this stream was researched across two distinct stretches: erosive and accumulative, which differ in the conditions for the hyporheic zone's interaction with the riverbed. The nutrients are delivered to the stream mainly in the erosive stretch and are related to the inflow of nutrient-rich groundwater from the urbanised catchment. The pollutants transported down by the stream are then delivered to the HZ in the accumulative stretch, where nitrates are denitrified and phosphates are deposited with the suspension. Ammonium nitrogen, in turn, is introduced into the stream from the HZ as a result of either the process of ammonification of organic matter deposited in sediments or inflow with polluted groundwater. The results indicate that the winter season is the most important period in shaping the interaction of river waters with the underlying hyporheic zone, in which the causal side of the relationship should be associated with the subchannel environment, and the effects are recorded in the river waters.

Keywords: headwater stream, hyporheic zone, nutrients, suburban area, vertical hydraulic gradient

INTRODUCTION

In the upper parts of river basins, small watercourses are under the influence of the hyporheic zone (HZ), which is one of the most important factors determining the chemical composition of river waters (Harvey et al. 2019). In relatively steep and shallow flowing streams, topography associated with pools and riffles and the meandering channel planform is one of the principal drivers of hyporheic flow (Harvey & Bencala 1993, Woessner 2000, Tonina & Buffington 2009). According to Wondzell (2011) head watercourses are not physically constrained in the same way as lowland rivers. In lowland rivers, the impact of the HZ on the transport of dissolved substances

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through river channels is limited by the coexistence of three basic circumstances: the lower permeability of bottom sediments, smaller transverse and longitudinal slopes of the valley, and higher channel flows. According to Harvey et al. (2019), the degree of connectivity between the two aquatic environments is important and directly affects the quality of the river downstream. Specifically, too little connectivity reduces the amount of river water exchanged and leads to biochemically inactive water being stored in the HZ; conversely, too much connectivity shortens the time for which water is in contact with streambed sediments and thus the potential for chemical reactions to take place there. According to Ward et al. (2012), there are three main determinants of hyporheic exchange, i.e. watercourse morphology, geological conditions of the bedrock of the riverbed, and the strength of hydraulic gradients. Larkin and Sharp (1992), meanwhile, indicate that the three main determinants are the width and depth of the channel, the slope of the alluvial valley floor, and the permeability of the riverbed bottom sediments. Extensive spatial analyses (Harvey et al. 2019) have shown that, in areas with moderately steep slopes and coarse sediments (i.e., bottom material with relatively high hydraulic permeability and sufficient time for water-sediment interaction), the role of the HZ is significant. This stands in contrast to rivers flowing down valleys with low slopes and with fine-grained bottom material in the channels, where the hyporheic flow is much smaller and the zone's hydrochemical role is much lower. This analysis shows that the potential significance of HZ reactivity for river water quality is the greatest for watercourses of the fourth order and smaller. Such watercourses, which are elementary parts of the river network, are relatively steep and shallow, and the topography of their valleys is associated with the alternating presence of pool stretches and gorge stretches. Both these and rivers with many meanders activate hyporheic flow (Harvey & Bencala 1993, Woessner 2000, Gooseff 2010, Krause et al. 2022). River water generally enters hyporheic flow paths where the slope is steep and then returns to the channel in sections with reduced river slope (Gooseff et al. 2006, Lautz et al. 2006, Marzadri et al. 2010, Sawyer et al. 2012). Model studies have shown that the depths to which the hyporheic flow reaches and the times of water residence on its paths are determined by the size of topographic features of the riverbed and the variability of the permeability of alluvial sediments (Woessner 2000, Wörman et al. 2007, Sawyer & Cardenas 2009). Hester and Doyle (2008) showed that the size of the drainage of groundwater to the river channel and the hydraulic permeability of bottom sediments are the most important factors determining hyporheic exchange, followed by the type of hydromorphological form (i.e., sills, weirs, rapids) and the thickness of the aquifers cut by the valley and its decline.

The river valley contains two separate interfaces: (1) the upland-riverbank interface, where groundwater runoff from supply areas towards valleys dominates, and (2) the streamside interface, in which the movement of water and dissolved substances is bi-directional and strongly influenced by channel hydrodynamics (Triska et al. 1993a). Such an upland-riverbank system consists of two zones, between which there is a sharp transition in terms of the many properties important to the biogeochemistry of the riverbed and its immediate underground environment. In most watercourses, there is a change from a well-mixed, oxygenated and day-lit river water environment that is relatively fast in transport, to a chemically reduced environment in constant darkness and with limited groundwater transport. Hyporheic exchange changes the physical and chemical conditions of the components of river waters and groundwaters quite drastically during the mixing of waters in the bottom sediments. Fluvial sediments are typically highly permeable, in contrast to calm sedimentary environments, and a wide variety of hyporheic exchange mechanisms produce HZ hydrochemical anisotropy on multiple scales. Ward (2012) and Zimmer and Lautz (2014) drew attention to another important factor shaping this anisotropy, i.e. the varying efficiency of mixing river waters and groundwater beneath the riverbed. In general, the transition from geologically dominated processes in the near-stream subsurface to hydrologically dominated processes takes place in the valley bottoms of headwater streams (Ward et al. 2016).

The main goal of the work is to assess the impact of the HZ on the hydrochemical state of the Malina, a small spring watercourse in the Łódzkie Hills area, with particular emphasis on the conditions of water exchange between the riverbed and its HZ. The short course of this stream has unique potential, in that two distinct stretches can be identified that may differ in the conditions for the hyporheic zone's interaction with the riverbed. Its course, morphology, and the nature of the bottom sediments provide the basis for distinguishing an erosive stretch and an accumulative stretch of similar lengths to one another; these are analogous to the gorge and pool stretches of a river valley. Between them, according to Wohl et al. (2015), there is a change from a "sediment translocation" regime to a "sediment deposition" regime, which may result in changes in the volume of hyporheic flow. This is followed by the following more specific questions:

– Are there significant differences in the hyporheic exchange flows between these stretches?
– How does this influence the potential for pollutants in the watercourse to be neutralised?

Particularly important in this respect seem to be biogenic compounds that are supplied to the geochemically anisotropic HZ environment with groundwaters and river waters and may undergo transformations there that determine their further migration in the aquatic environment. According to Arnon et al. (2013), the HZ has great potential to regulate the existence of nitrates in streams, and although Cirmo and McDonnell (1997) cite the HZ as one of many "around-stream" zones with such capabilities, it is relatively little understood. However, it must be said that rapid progress has been made on this topic in recent years (Boano et al. 2014, Lewandowski et al. 2019, Krause et al. 2022).

STUDY AREA

Morphology and hydrography

The Malina is part of the Bzura basin; it is a right-bank tributary of the Dzierżązna river and is approximately 1.400 m long (Fig. 1). In the structure of the river network, it is a 6^{th}-order stream (Grulke & Ziułkiewicz 2022).

According to the digital elevation model (geoportal.gov.pl.), the initial spring of the Malina is located at an altitude of 183.5 m above sea level (a.s.l.). The catchment area of the Malina zero runoff is relatively small in comparison to other elementary watercourses in the Łódź Hills (Moniewski 2004). The local drainage pattern is dendritic-radial and generally directed northwards; it was formed by the intensive drainage of a small fluvioglacial plain located within the second (Smardzew) edge level of the Łódź Upland (Klatkowa 1993). This plain is cut latitudinally to the south by the Bzura river valley, and to the north it rests on a series of moraine hills and descends to the north with a long slope to the lower, third (Stryków) edge level. Within this slope, the Malina has created a deep, straight, consistent valley. The height differences between its bottom and the culmination of the adjacent moraine hills reach 20 m. The Malina flows within a feature of the edge relief between the culminating zone of the Łódzkie Hills and its south-western foreground, i.e. the Błońska Plain. The upper part of the Malina valley, above the "Malinka" resort, was partly designated for the construction of small retention reservoirs, serving as sedimentation tanks protecting against the flow of pollutants down from the Zgierz-Rudunki housing estate. The first reservoir, Rudunki II (A = 0.18 ha, V = 4.028 m^3, maximum water damming (max.w.d.) = 183.2 m a.s.l), separates the river from its initial spring, and the two forest ponds (ΣA = 0.47 ha, ΣV = 5.400 m^3, max.w.d. = 174.9 m a.s.l.) start a cascade of five reservoirs of various capacities and functions that occupy the entire lower part of the Malina valley until its connection with the Dzierżązna valley (Fig. 1C). The construction of reservoirs in the lower part of the valley, and thus the elevation of the erosion base, slowed the deep erosion and caused the valley to begin filling with material transported from its upper part, partially bounded by the presence of the Rudunki II reservoir. This process is evidenced by the transverse hypsometric profiles of the valley (Fig. 2). A probing of the Malina riverbed bottom in the accumulative section showed the existence of a "hard", primal bottom of the watercourse, which in the depth progression fits the profile of the upper erosive stretch.

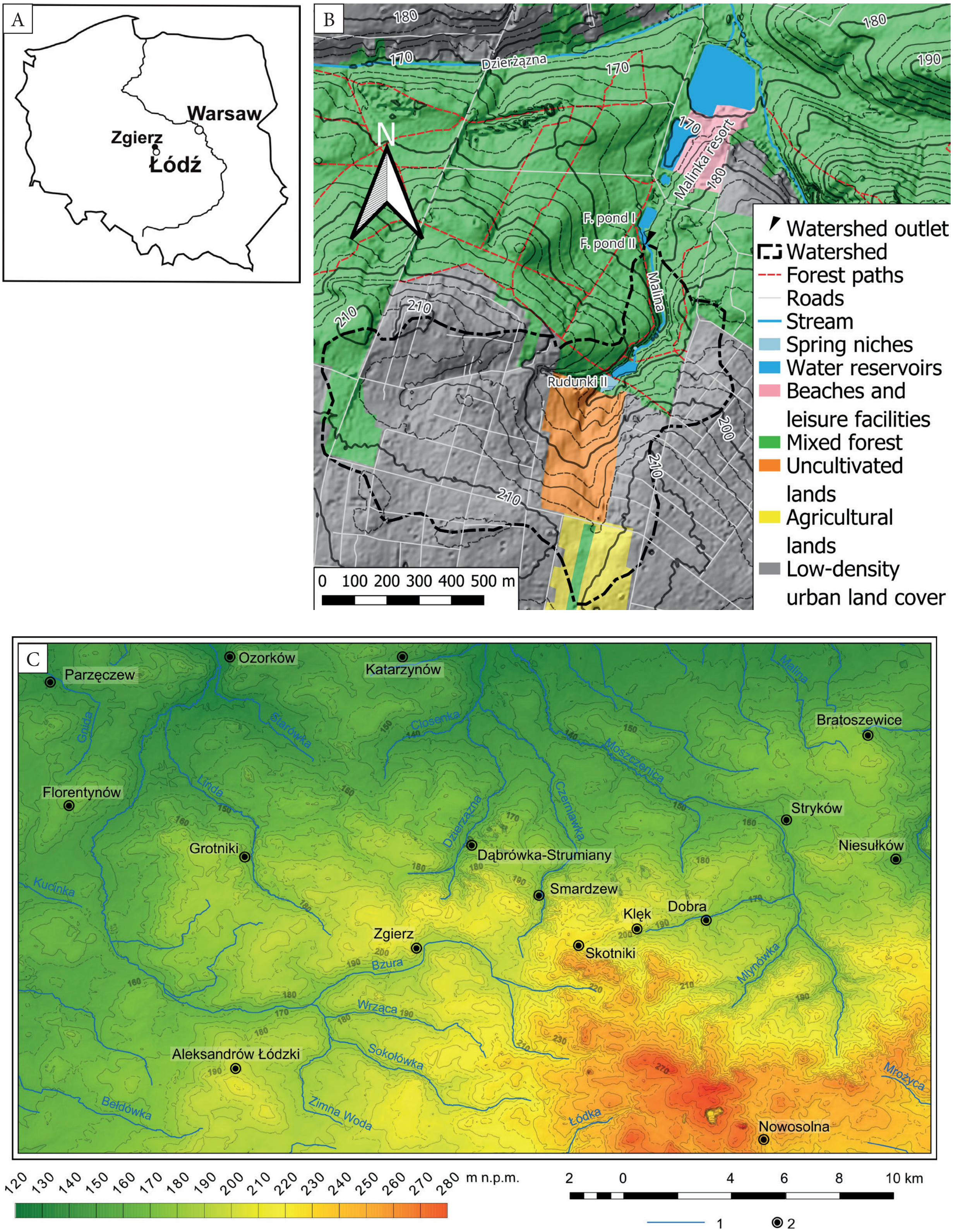

Fig. 1. Location of the research area in Poland (A) and in the upper part of the Bzura catchment (B) (1 – streams and rivers, 2 – cities and villages); morphology and land use of the Malina catchment (C)

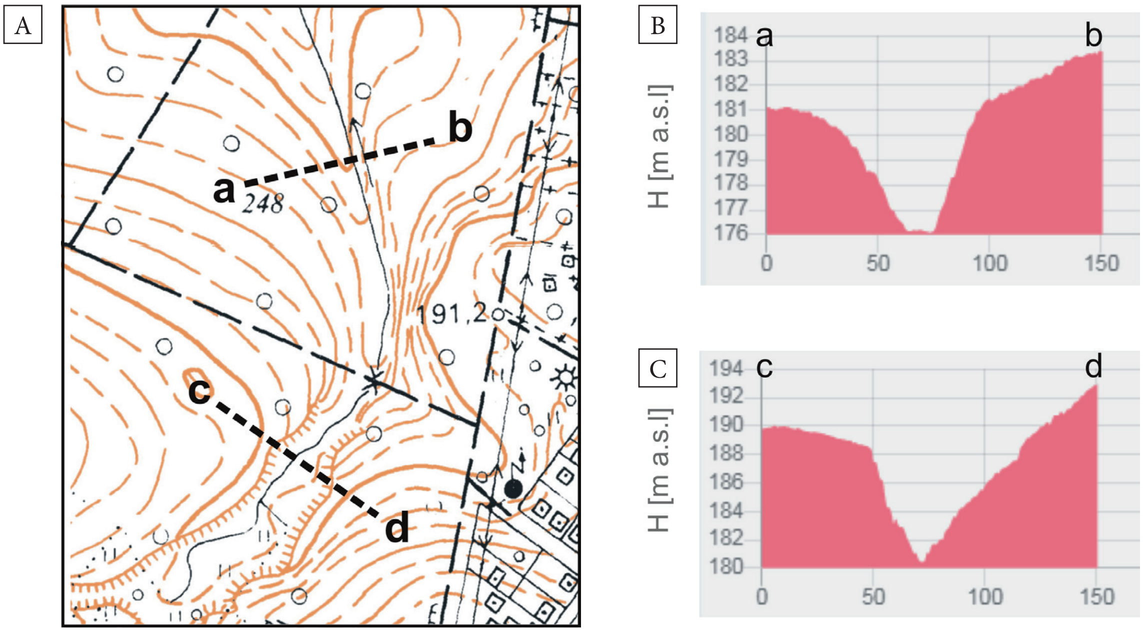

Fig. 2. Hypsometric profiles of the Malina valley according to digital elevation model: *A)* layout of profiles; *B) profile of accumulative stretch; C) profile of the erosive stretch (topographic map to scale 1:10 000; geoportal.gov.pl)*

Hydrogeological condition

The Malina is supplied by two natural springs, the initial Rudunki-1 located slightly above the backwater of the Rudunki II reservoir and the Rudunki-2 (Ru-2) spring (Fig. 1C) located below the dam of this reservoir in a niche formed within the western valley slope. Behind them, along the course of the riverbed and at the external edge of a narrow flood terrace, there are a great number of linearly arranged seepages and leakages. The watercourse drains a thicker sandy fluvioglacial structure that reaches the top of the Upper Cretaceous carbonate formations (Klatkowa et al. 1995). The aquifer is not isolated from the land surface and the water table is stable within the plateau at ordinates of 185–190 m a.s.l., i.e. at the depth range of 10–20 m below ground surface. The outflow of groundwater is northwards and drains into the Dzierżązna and Czerniawka valleys (Pęczkowska & Figiel 2006). In the recent past, the Malina catchment area was under the influence of increased groundwater extraction for the needs of the city of Zgierz. This activity resulted in a depression cone forming in the Upper Cretaceous sediments that extends laterally to this location (Meszczyński & Szczerbicka 2002). The southern part of the catchment was also covered by a depression cone formed in the Quaternary formations as a result of the nearby functioning of a municipal groundwater intake (Pęczkowska & Figiel 2006). Moniewski (2004) points out that the springs of the Dzierżązna (and of the Malina) are recharged from fluvioglacial sands and gravel formations underlain by moraine clays of the Warta stage (Saale glaciation). This relates to the Rudunki-2 ascending spring, whereas the Rudunki-1 layer spring is also recharged by waters inflowing from the south, as evidenced by the directions of development of back erosion and hence the clearly asymmetric shape of this niche (Grulke & Ziułkiewicz 2022).

Land use

The Malina valley is located within the wedge-shaped "Dąbrówka Municipal Forest" complex bounded to the south-east and south-west by single-family housing of the Zgierz-Rudunki estate (Fig. 1C). The Rudunki-1 spring is located on the southern border of a forest, and the niche itself extends as a dry valley among the buildings. The area of the Rudunki estate has a water supply system but no access to the municipal sewage network (Urząd Miasta Zgierza 2015). The rainwater drainage system covers only the eastern part of the estate and has an outlet in the valley of a nameless watercourse flowing into the Malina below the "Malinka" resort reservoirs. To the north-east, residential development gives way to recreation, so that the area of dispersed development accompanies the Malina to the resort facilities and is separated from the river by a narrow strip of forest covering the steep, eastern slope of its valley. The area of recreational development has a well-developed water supply network, but, similarly to the area of permanent housing development, there is no municipal sanitary sewage system, and residents use private solutions. In the extension of the Malina valley to the south of the Rudunki-1 niche, there are no permanent buildings (Fig. 1C), which means that in the absence of a rainwater drainage system and favourable terrain, rainwater and snowmelt flow from the estate in an unmanaged manner into this spring niche. Such periodic flows exist along the course of the Malina through ravines cutting the eastern slope of the valley and bring rainwater and meltwater from the area of the residential and recreational development.

METHODS

Hyporheic zone (HZ)

A gradientmeter was used to measure the vertical hydraulic gradient (VHG) between river waters and the HZ (Marciniak & Chudziak 2015). This device was modified in the Laboratory of Geology of the Lodz University, allowing it to also be used to collect water samples from the hyporheic zone. Measurements and samplings were carried out in three periods: in winter, on December 9–11, 2020, spring, on March 20–24, 2021 and summer, on June 20–23, 2021. In the first period, the conditions prevailing in the riverbed bottom were identified and the distance between measurement points was determined in the following seasons. All measurements with the gradientmeter were made along the axis of the watercourse, which was determined by the current, so they were always the deepest fragments of the bottom in a given cross-section of the channel.

Malina watercourse

Simultaneously with the HZ tests, the river flow was measured in four measurement profiles: the first (Ma-1) at the outlet of the initial spring niche and above the Rudunki II reservoir, the second (Ma-2) below the dam of the Rudunki II reservoir and upstream of the Rudunki-2 spring, the third (Ma-3) in the zone of refraction of the decrease in watercourse slope between the erosive and accumulative stretch of the Malina, and the fourth (Ma-4) at the end of the test section, above the backwater of forest pond II (Fig. 4). Depending on the prevailing conditions for measurement, a volumetric or field-velocity method was used to measure the flow, and, depending on local conditions, water velocity was measured using the float method or a Hega-2 hydrometric mill (Biomix, Poland). The physicochemical parameters of river water, spring water and waters collected with a gradientmeter were measured *in situ* in special overflow cell, which allow measurement temperature (T_W), pH-reaction, SEC and (in June 2021 only) redox potential[1]; CPC-411 and CX-742 meters (ELEMETRON, Poland) were used. Water samples for chemical analysis were taken in PE containers with a capacity of 500 mL for determination of mineral forms of nitrogen ($N\text{-}NH_4$, $N\text{-}NO_2$ and $N\text{-}NO_3$) and phosphorus ($P\text{-}PO_4$). Then, they were cooled and stored in a travel refrigerator at 4°C and delivered immediately after measurement to the laboratory of the Department of Geology and Geomorphology University of Lodz (DGG UL). Chemical analyses were performed with an ion chromatograph model S.330 (Marcel S.A., Poland) device and standard analytical kits[2]. In December 2020, 8 water samples were collected from the HZ, in March 2021 and

[1] Sensor bodies which are used with cell should have a fixed diameter (oxygen sensor type CTN-920S didn't fit for measuring cell).

[2] Phosphate concentrations according to PN-73 C-04537, ammonium according to DIN 38406-5, nitrates according to DIN EN 26777, nitrites according to DIN 38405-9 and Merck standard solutions.

June 2021, 9 samples each. In addition, 4 samples of river water were taken and one sample of spring water in each season. Water from the HZ was collected for analysis immediately after the VHG measurement in the upwelling sites, as the "upwelling" water may differ significantly thermally and chemically from the stream water (Wondzell 2011). Spring waters were considered to be representative of groundwater, because the Malina catchment has no facilities providing access to the surface-most aquifer. On the basis of river flow and nutrient concentration, their loads were calculated according to formula:

$$L\ [\mathrm{kg/h}] = Q\ [\mathrm{dm^3/s}] \cdot c\ [\mathrm{mg/dm^3}] \cdot 3.600 \quad (1)$$

The Malina riverbed bottom sediments were collected at 13 sites with a manual drill in a casing pipe from a maximum depth of 25 cm in places where the VHG measurement had previously been made. These samples were subjected to granulometric analysis in the laboratory of the DGG UL using the sieve method (Mycielska-Dowgiałło 1995) and to the analysis of organic carbon content at the Department of Physical Geography UL laboratory using the Tiurin method (Brogowski & Czerwiński 1973). The results of the granulometric analysis were used to, for example, calculate the permeability coefficient (*k*) using the USBCS method (Pazdro & Kozerski 1990). This made it possible to calculate the filtration time of river waters through the HZ of the Malina in sections selected on the basis of the VHG measurement results. A formula derived from Darcy's law was used:

$$T_{\mathrm{HZ}} = \left(\frac{l}{k_{10}}\right) \cdot i \quad (2)$$

where:

- l – distance between adjacent downwelling and upwelling measuring points [m],
- k_{10} – average permeability coefficient of HZ formations in a given section [m/d],
- i – hydraulic gradients between downwelling and upwelling measuring points [cm/cm].

To assess the hydrochemical similarity of the studied waters, the cluster analysis was used with grouping of cases by Ward's method in Euclidean space. Calculations were made in the Statistica 13.1 program after prior data standardisation.

RESULTS

The Malina begins its course from the vast spring niche of Rudunki-1, where groundwater appears on the niche bottom in the form of dispersed outflows. After a few metres, the spring waters go to the Rudunki II reservoir. Below the reservoir dam, rapid flow of water begins along the riverbed, with velocities of 0.19–0.37 m/s; below, where the riverbed is narrower, it reaches 0.31–0.51 m/s; in the accumulative stretch it decreases up to 0.21–0.29 m/s. The Reynolds number (Klimaszewski 1981) at the exit (the Rudunki-1 niche) and at the closure of the research section (Ma-4) was R_e 166–213 and 172–277, respectively. These numbers indicate that conditions favour laminar flow in the riverbed and turbulent flow in the erosive stretch (between Ma-2 and Ma-3), at R_e 522–649. Water velocities in the Malina riverbed (highest in March 2021, at 0.20–0.51 m/s) were conducive to removing material ranging from the sand fraction (0.5 mm) to gravel (2.5 mm) from the bottom (Klimaszewski 1981) by contrast, in the winter season, the runoff of water at velocities of 0.19–0.31 m/s was not sufficient to remove material of $d > 0.75$ mm from the river bottom.

Table 1 contains a summary of the significant characteristics of the distinguished stretches of the Malina watercourse and its entirety, i.e. from sampling points Ma-1 to Ma-4.

In the scope of the data compiled (Table 1), the erosive and accumulative stretches differ fundamentally in terms of the watercourse's longitudinal gradient, the characteristics of riverbed sediments, and the value of the k_{10} permeable coefficient (Fig. 3C). This, in turn, is reflected in the HYP_{POT} value, which indicates that the hyporheic exchange potential is an order of magnitude higher for the erosive stretch than for the accumulative stretch.

The river flow at the end of the research section (Ma-4) ranged from 5.4 to 2.8 dm^3/s. The most water flowed in spring and the least in summer. The flow between these seasons decreased by 48%, although the supply structure of the watercourse was maintained with 28% of water flow in the channel in the accumulative stretch. In December 2020, this share was higher, slightly exceeding 40%.

Table 1
Hydrological and morphological characteristics of researched stretches of the upper Malina on the basis of average values from measuring points

Parameter	Erosive stretch	Accumulative stretch	Malina river
Length of watercourse [m]	235	192	427
Lenght of valley* [m]	215	161	377
Tortuosity of the watercourse	1.09	1.19	1.13
Slope of the watercourse [‰]	22.1	6.6	13.7
River flow (*Q*) [dm^3/s] – change after passing the accumulative stretch			
XII 2020	2.9	+2.0	4.9
III 2021	3.9	+1.5	5.4
VI 2021	2.0	+0.8	2.8
k_{10} [m/d] / S*n* = 13	8.62	4.71	6.67
/Me/U [–]	8.45	2.80	3.63
HYP_{POT}** [–]	3.31E-04	3.69E-05	1.71E-04
C_{org} [%] / S*n* = 13 mean (max-min)	0.36 (0.08–0.66)	0.17 (0.03–0.37)	0.27
Mean value of VHG* [cm/cm]**			
XII 2020 / S*n* = 68	+0.184	−0.024	+0.071
III 2021 / S*n* = 35	+0.079	+0.029	+0.056
VI 2021 / S*n* = 36	+0.019	−0.082	−0.046

* to the Rudunki II reservoir's dam,
** acc. to Wondzel (2011),
*** positive value means upwelling and negative value means downwelling.

Figure 3 presents the results of VHG measurements in three seasons based on the longitudinal profile of the Malina research section. In December 2020, high positive gradients (upwelling) generally occurred in two places located on the erosive stretch. The first one, going from the upper part of the valley, is near the Ru-2 spring and is a section of the riverbed below the Rudunki II dam. The second such place is located at the upper part of the erosive stretch, where the hydraulic gradient exceeded the value measured directly in the ascension groundwater outflow at the bottom of the Ru-2 spring niche. Between these places, the hydraulic gradients were much smaller and had different directions, including three cases of pressure equilibrium (gradient: 0 cm/cm). In the accumulative stretch, cases of negative gradients (downwelling) clearly dominated over positive ones, which were generally of smaller magnitude.

In March 2021, both places of positive gradients in the erosive stretch were still visible, but were not as strong as three months earlier, and the zone of strong upwelling on the border of the erosive and accumulative stretches retreated slightly towards the upper part of the valley. Compared to December 2020, the phenomenon of downwelling intensified in the central part of the erosive stretch and clearly weakened in the accumulative one, while the general strength of upwelling increased.

In June 2021, the upwelling zones in the erosive stretch clearly weakened; the upper one dissipated, and the lower one receded even further towards the upper part of the valley. In the middle part of the erosive stretch, downwelling clearly intensified compared to previous measurement seasons. In the accumulative stretch, the phenomenon of downwelling also gained strength, both in terms of the number of detected cases and the strength of the negative gradient, clearly exceeding cases those found earlier.

The strength and direction of the VHG indicate permanent upwelling in the erosive stretch (although this is nearly ten times weaker in summer than in winter) and downwelling in the accumulative stretch (except in spring, when upwelling was dominant here as well) (Table 1) In the scale of the entire Malina research section, the mean hydraulic gradients indicate that the conditions for drainage of water from the HZ were best in December 2020 and worse in March 2021, whereas conditions in June 2021 favoured the infiltration of stream waters into the HZ, especially in the accumulative stretch.

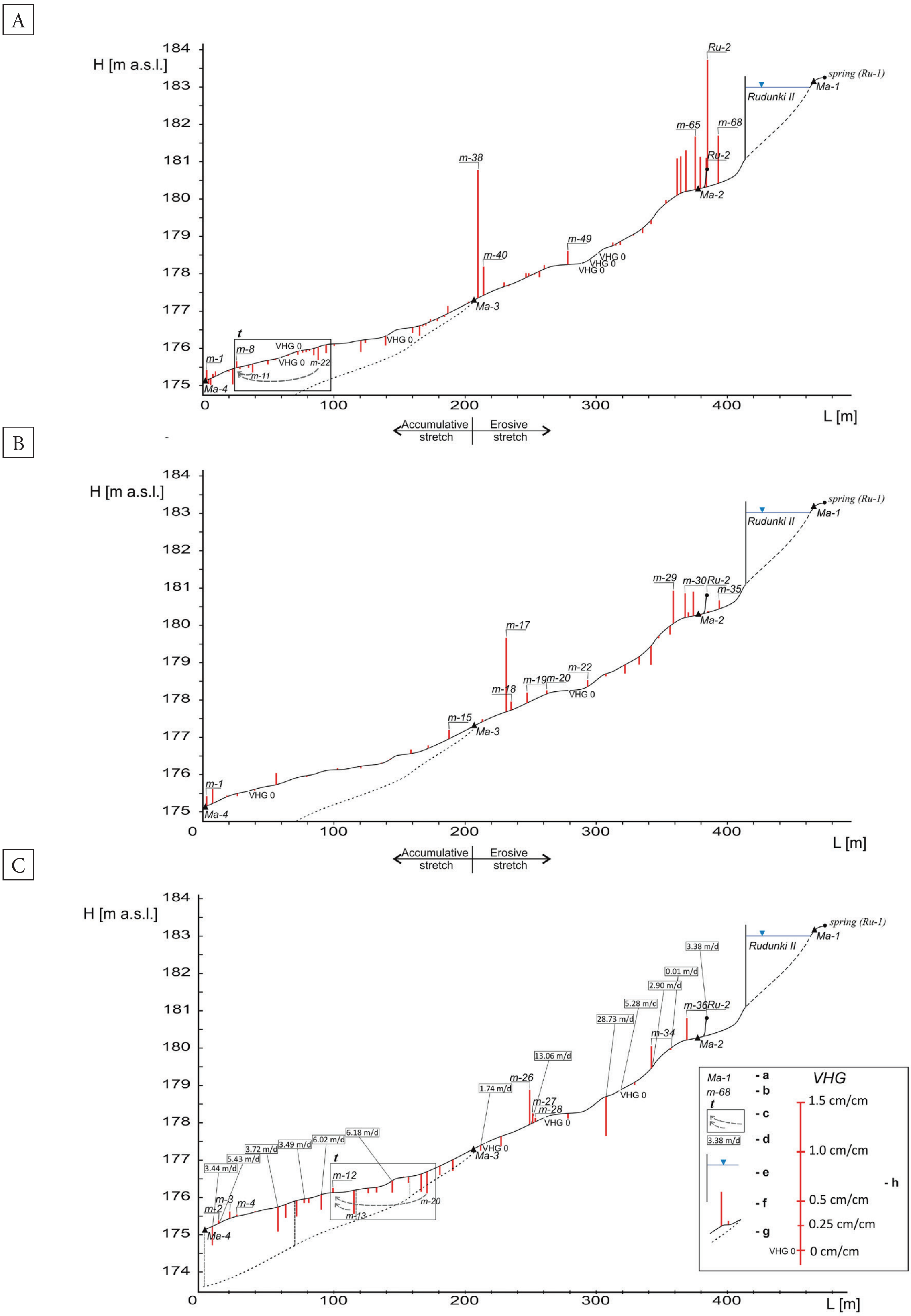

Fig. 3. *Malina watercourse measurement profiles in three research seasons: A) December 2020; B) March 2021; C) June 2021; a – measuring point on the stream, b – point of hyporheic water sampling, c – section on which the filtration time of river waters by HZ was calculated, d – permeable coefficient (k) of the Malina bottom sediments, e – retention reservoir, f – VHG measurement locations with its size (comparative measurement scale beside), g – buried valley floor*

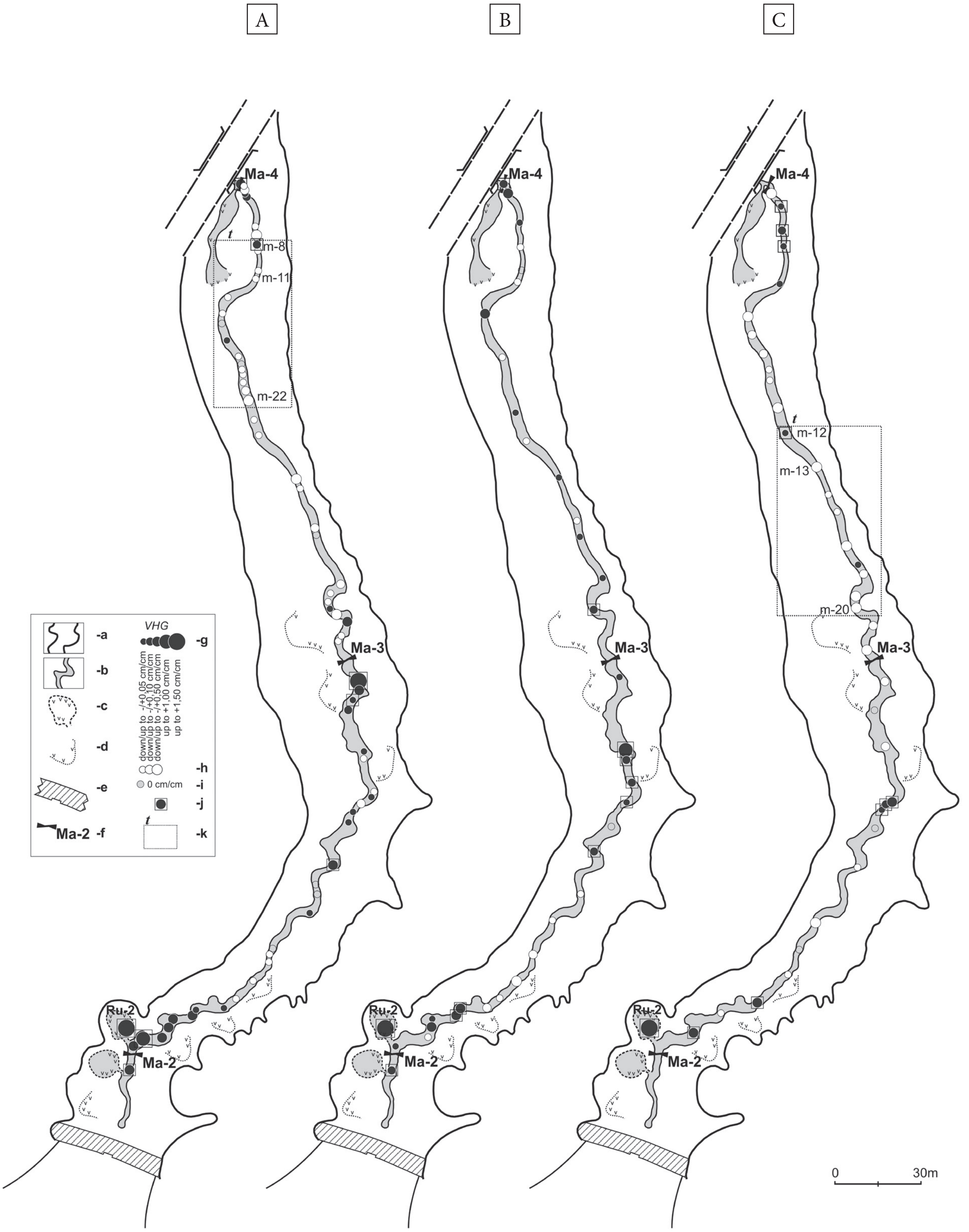

Fig. 4. *Values of VHG measured in the Malina riverbed bottom in three research seasons: A) December 2020; B) March 2021; C) June 2021; a – edges of the valley, b – Malina riverbed, c – spring niche, d – leakage zone by the channel, e – Rudunki II reservoir dam, f – research point on the stream, g – upwelling with scaled VHG value, h – downwelling with scaled VHG value, i – VHG equal zero, j – sampling point of hyporheic waters, k – section on which the filtration time of river waters by HZ was calculated*

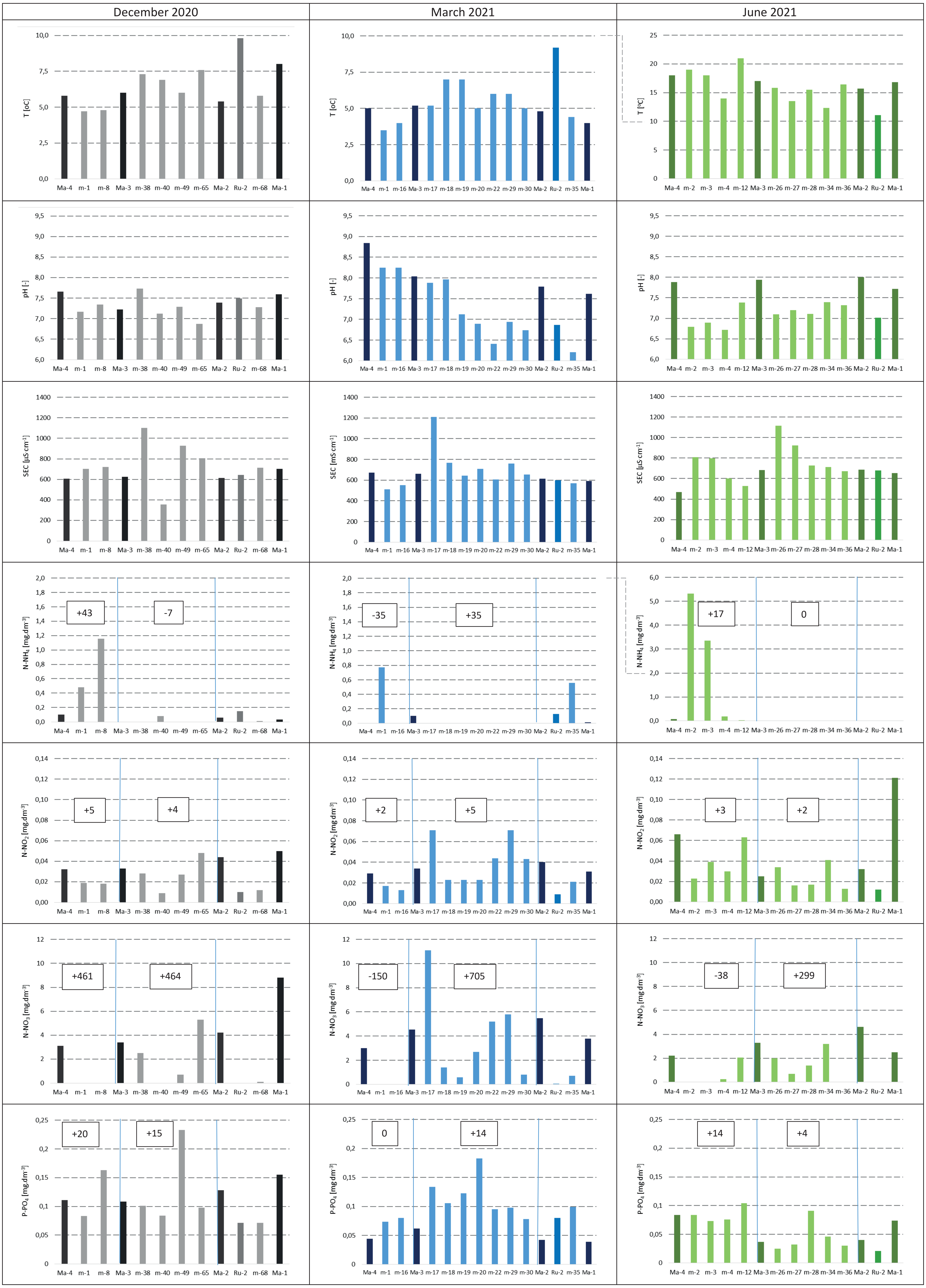

Fig. 5. Hydrochemical properties of the researched waters in the Malina valley in three measuring seasons and the changes of nutrient load flowed down through separated stretches of the stream (in boxes) according to Table 2

Physical and chemical properties of the Malina river waters and hyporheic waters

The hydrochemical data collected in three research seasons are summarised in Figure 5 (on the interleaf). They cover waters of the Malina (Ma-1, Ma-2, Ma-3, and Ma-4), hyporheic waters obtained in places of their upwelling, and spring water from the Ru-2. The temperature of the hyporheic waters in the erosive stretch in winter and spring was higher than in the Malina stream waters, although not as high as in the Ru-2 niche, whereas in the accumulative stretch it was generally lower. In summer, the situation changed: in the erosive stretch, the temperature of hyporheic waters was similar to the Malina stream waters or slightly lower, but higher than the spring waters. This happened when downwelling intensified in this stretch (Figs. 3C, 4C). In the accumulative stretch, the hyporheic waters turned out to be slightly warmer than the waters of the stream itself in June 2021.

In winter, the pH-reaction of the hyporheic waters was lower than that of stream and spring waters. In March 2021, in the erosive stretch, the pH of hyporheic waters was close to that of the spring waters; however, beginning from the boundary zone where the erosive stretch ends and the accumulative stretch begins, the pH increased, as did the pH of the Malina stream waters. The regularity of this phenomenon through geographical space may indicate that this is not the result of infiltration of river waters (downwelling), but the appearance in the hyporheic zone of an accumulative stretch of groundwaters with a higher pH and their impact on the pH of the stream. In general, the pH of hyporheic waters in March 2021 varied widely from 6.21 to 8.25 with a constant rising tendency downwards through the valley, which also relates to the course of the stream waters. In June 2021, the pH-reaction of spring and hyporheic waters was lower than that of stream waters, while it was lowest in the accumulative stretch and highest in the erosive stretch.

In terms of SEC, the hyporheic waters of the erosive stretch generally stood out positively compared to the other water environments. In the accumulative stretch, SEC was higher in the hyporheic waters than in the stream in December 2020 and lower in March 2021. In June 2021, SEC in both waters (HZ and stream) were mirror reflections of one another along the course of the Malina – as one increased, the other decreased. In the measuring series of June 2021 the SEC of hyporheic waters general increased along the course of the Malina (from the first of the sampling points to the last). Conversely, in the same data series, the SEC of the stream waters decreased in the same order – from the springs to the end of the research section (Fig. 3).

Ammonium nitrogen emphasises the hydrochemical peculiarity of hyporheic waters of the accumulative stretch in all research seasons. $N\text{-}NH_4$ concentrations there were many times higher in the HZ than in the spring waters or stream waters, which is so important due to the nature of water exchange in this stretch of the riverbed. $N\text{-}NH_4$ was only recorded in the stream locally and at a relatively low concentrations, being lower than in spring waters.

Nitrite nitrogen was a very variable parameter over the study area and study period. In December 2020, concentrations were generally lower in hyporheic waters than in the stream. There was clear increase in $N\text{-}NO_2$ concentrations in the HZ waters in March 2021 in a part of the erosive stretch, and it exceeded the level recorded in the Malina. By contrast, in the accumulative stretch, the concentration level of $N\text{-}NO_2$ in hyporheic waters increased in June 2021 and it accompanied locally high concentrations nitrites in the stream (Ma-1 and Ma-4). In all seasons, the level of $N\text{-}NO_2$ recorded in spring waters was generally lower than in hyporheic waters.

Nitrate nitrogen, similarly to ammonium nitrogen, was not recorded in all environments: it was absent in spring waters in winter and summer, and in several sampling points of hyporheic waters – basically in the accumulative stretch. $N\text{-}NO_3$ generally remained at a higher concentration in the stream than in hyporheic waters. The erosive stretch stood out very clearly, especially in March 2021, when nitrate nitrogen concentrations in several cases exceeded the level recorded in the Malina proper.

Phosphate phosphorus, as in the case of $N\text{-}NO_3$, clearly distinguished the hyporheic waters of the erosive stretch in March 2021. At that time, its concentrations in spring waters and hyporheic waters were higher than those found in the waters of the Malina. In June 2021, $P\text{-}PO_4$ distinguished the hyporheic water of the accumulation stretch (similarly as with N-NH_4 and N-NO_2) but its concentration never dropped to zero anywhere. In December 2020, the situation was very dynamic: the Malina waters showed higher concentrations of P-PO_4 than did spring waters and hyporheic waters, except in two cases – one each from the erosive and accumulative stretches. None of these peculiarities was reflected in the picture of spatial variability of other hydrochemical compounds.

The cluster analysis of the hydrochemical characteristics of the researched waters is presented in Figure 6. In December 2020, the Malina waters showed numerous cases of strong similarity to the hyporheic waters. Notably, the pair of points Ma-3 and m-38 are very similar to one another and stand out markedly from the other points. The same is true (standing out even more markedly, in fact) of Ma-1, Ru-2 and m-65. The third group is Ma-2 associated with m-68 and Ma-4 with m-8. These two pairs are joined by further linkage of water with the HZ captured at more distant points along the course of the Malina (Fig. 3A). In March 2021, surface waters formed an entirely separate group that includes HZ waters from the accumulative stretch (m-15) and a weak pair of points m-1 and m-35 (i.e. from the beginning and the end of the studied river section). Waters from m-17 are characterised by a clear hydrochemical distinctness and very poor statistical hydrochemical similarity with the other cases of hyporheic waters of erosive stretch and spring waters (Ru-2). In June 2021, the Malina waters maintained their hydrochemical difference from the HZ waters and spring waters, with the exception of two cases: m-12 and m-34. All the other points formed a second group that included spring waters and hyporheic waters of both stretches of the Malina.

Nutrient loads flowing through both stretches of the Malina river are compared with the values of average VHG in Table 2. Looking at these two datasets, it can be noted that:

- in the erosive stretch with permanent upwelling, the nutrient loads increased (Ma-3),
- in the accumulative stretch, loads increased with downwelling, but in March 2021 when upwelling occurred, the loads of N-NH_4 and N-NO_3 decreased or did not change (P-PO_4).

Table 2
Nutrient loads flowing down the Malina between separated stretches versus mean hydraulic gradients in the riverbed bottom

Sampling point	Load [g/h]				Load change [g/h]				Mean VHG [cm/cm]	
	N-NH_4	N-NO_2	N-NO_3	P-PO_4	N-NH_4	N-NO_2	N-NO_3	P-PO_4	In stretch*	Malina
December 2020										
Ma-2	0.29	0.17	16.18	0.49	–	–	–	–	0.184	
Ma-3	0.00	0.34	35.50	1.13	−0.29	+0.18	+19.32	+0.63		0.071
Ma-4	1.80	0.56	54.68	1.96	+1.80	+0.22	+19.18	+0.83	−0.024	
Δ*L*					+1.51	+0.40	+38.50	+1.46		
March 2021										
Ma-2	0.00	0.26	35.21	0.27	–	–	–	–	0.079	
Ma-3	1.47	0.48	64.58	0.87	+1.47	+0.22	+29.37	+0.60		0.056
Ma-4	0.00	0.56	58.32	0.86	−1.47	+0.09	-6.26	−0.01	0.029	
Δ*L*					0.00	+0.31	+23.11	+0.59		
June 2021										
Ma-2	0.00	0.08	11.32	0.10	–	–	–	–	0.019	
Ma-3	0.00	0.18	23.76	0.27	0.00	+0.10	+12.44	+0.17		−0.046
Ma-4	0.71	0.32	22.18	0.85	+0.71	+0.14	−1.58	+0.58**	−0.082	
Δ*L*					+0.71	+0.24	+10.86	+0.75		

* The upper of the given values applies to the erosive stretch between Ma-2 and Ma-3, and the lower value, the accumulative stretch between Ma-3 and Ma-4.

** See Table 3.

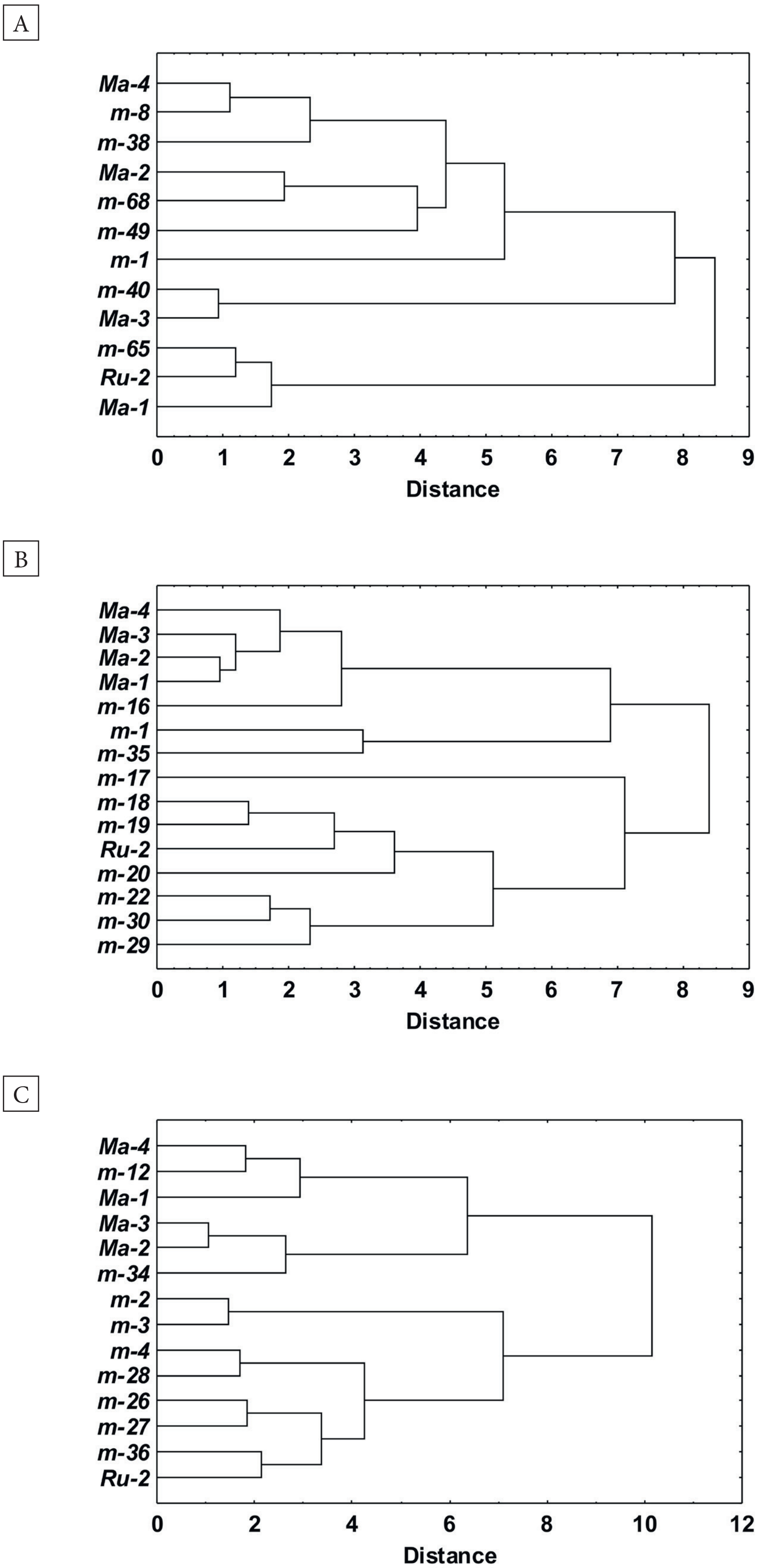

Fig. 6. *Hydrochemical similarity assessment of water sampling points in the Malina valley on clustering diagrams for each of research period: A) December 2020; B) March 2021; C) June 2021*

Changes in the loads of nutrients flowing down through both stretches of the Malina (Table 2) are shown in relation to the chemical composition of all researched waters in Figure 5 (on the interleaf). The increased load of N-NH_4 on the accumulative stretch in December 2020 and June 2021 seems be caused by its "delivery" from the HZ. In March 2021, the situation was complex, because the load in the erosive stretch increased significantly despite no zones having been identified where this mineral form of nitrogen upwelled to the riverbed. By contrast, the load in the accumulative stretch was balanced to zero, despite the recognised nitrogen supply from the HZ. In March 2021 the river waters were hydrochemically more distinct than spring and hyporheic waters (Fig. 6B). Under early spring conditions, other catchment factors such as surface and subsurface runoff determine the chemical state of the stream. Nitrite nitrogen loads do not seem to be related to the concentrations recorded in upwelling waters on the erosive stretch, although they may have contributed N-NO_3 to the riverbed due to a further stage of NO_2^- nitrification. This hypothesis was not confirmed in June 2021 in the accumulative stretch, where, despite the increase in the N-NO_2 load "supported" by the delivery of nitrites from the HZ, the N-NO_3 load was significantly reduced. An even stronger reduction in nitrate nitrogen was marked in this stretch in March 2021, when N-NO_3 was not delivered from the HZ with the simultaneous reduction in the charge of its "precursor", i.e. N-NH_4. On the erosive stretch, the concentrations of nitrate nitrogen in the upwelling waters were constantly high, which is reflected in a strong increase in the load of nitrates carried in this stretch of the Malina, especially in March 2021, when N-NO_3 in hyporheic waters also reached maximum concentrations. A similar situation applies to P-PO_4, whose changes in load on both stretches are also related to the concentrations of these in the upwelling waters, especially in March 2021 and June 2021.

The balance of nutrient loads flowing down the Malina between sampling points Ma-2 and Ma-4 (Table 2) indicates that, with one exception, they rose. The increase in nutrients was largest for N-NO_3 in the erosive stretch (from Ma-2 to Ma-3), while the load of P-PO_4 and N-NH_4 increased systematically along the course of the accumulative stretch (Ma-3 to Ma-4). It is generally clear that, along with the decrease in VHG size and the transition from winter to summer from upwelling to downwelling, there was a clear decrease in the load of nitrate nitrogen carried by the Malina to reservoirs.

On the basis of the collected data, a simulated calculation of the flow time of the river waters through the HZ was made, assuming two scenarios: 1. flow between the point of strong downwelling and the nearest upwelling point (Fig. 3A, C); 2. flow between the point of strong downwelling above the meander bend (Fig. 4A) and the same point of upwelling as in scenario 1. The results of the calculations were confronted with the changes in the concentrations of mineral forms of nitrogen and phosphorus in river waters on a "trip" to the HZ. For the calculations, points were selected where there was a strong hydrochemical similarity of HZ waters with river waters (Figs. 3A, C, 6). Such cases occurred in December 2020 and June 2021. For March 2021, the simulation was not performed, as the Malina waters generally showed a weak similarity to hyporheic waters. The calculation results are presented in Table 3.

The short sections of riverbed for which calculations were performed do not overlap one another. For December 2020, one is located lower on the watercourse (Figs. 3A, 4A) than the segment for June 2021 (Fig. 3C). In the first period, the section of the riverbed bottom with a higher content of organic carbon (C_{org}) was filtrated by cool waters not containing N-NH_4, but with N-NO_3 (at levels so high that they are off the scale for classification of water quality for a sandy lowland stream according to Regulation of the Minister of Infrastructure (Rozporządzenie 2021). After a maximum of 2.5 days, the concentration of the first form of nitrogen clearly increased (to non-classified water-quality levels), the N-NO_3 completely disappeared; the concentration of P-PO_4 increased and the concentration of N-NO_2 decreased by half. In June 2021, downwelling was stronger than upwelling. In these conditions, the riverbed bottom sediments, which were lower in C_{org}, were penetrated by river waters. Compared to December 2020, these waters are much warmer, similar in nitrate nitrogen, slightly lower in N-NO_2, and markedly lower in P-PO_4.

Table 3
Calculations of concentration changes biogenic compounds during river waters filtration through HZ for the conditions of December 2020 and June 2021

Parameter	December 2020			June 2021		
	from m-22 [Ma-3]* ↓	from m-11 [Ma-3] ↓	to m-8 ↑	from m-20 [Ma-3] ↓	from m-13 [Ma-3] ↓	to m-12 ↑
T_W [°C]	6.0		4.8	18.0		17.0
C_{org} [%]	0.17–0.37			0.15–0.21		
i [cm/cm]	−0.065	−0.025	+0.065	−0.220	−0.235	+0.045
T_{HZ} in the 1st scenario [day]	–	0.18		–	0.74	
T_{HZ} in the 2nd scenario [day]	2.50			3.08		
$N\text{-}NH_4$ [mg/dm³]	0		1.159	0		0.022
$N\text{-}NO_2$ [mg/dm³]	0.033		0.018	0.025		0.063
$N\text{-}NO_3$ [mg/dm³]	3.40		0	3.30		2.07
$P\text{-}PO_4$ [mg/dm³]	0.108		0.163	0.037		0.104

* Nutrient concentrations in downwelling river waters were assumed according to Ma-3 sampling point on Malina.

After a maximum of three days, waters with a small amount of $N\text{-}NH_4$, a slightly reduced amount of $N\text{-}NO_3$ (except in class-2 quality waters) and clearly increased concentrations of other mineral forms of nutrients penetrated the Malina riverbed.

DISCUSSION

The morphology of the Malina valley developed in the highest, north-western part of the Łódź Hills and gives grounds for distinguishing three characteristic sections of the riverbed: 1) initial, within the Rudunki-1 niche, where groundwater outflow is generally dispersed and surface outflow from the spring niche to the riverbed is concentrated; 2) erosive, where water flows in a turbulent motion, launching a thicker fraction from the bottom; 3) accumulative, where the movement of water in the riverbed is more laminar, and the erosion capacity decreases with increasing sedimentation capacity. In terms of the granulometric structure of the Malina riverbed bottom formations, their ability to conduct water is "good" in the accumulative stretch and "good to very good" in the erosive one (Table 1). In general, the permeability conditions, expressed by the k_{10} coefficient, are very variable in the Malina section under study, which, in the opinion of Naranjo et al. (2013), is typical of a fluvial environment. Taking into account the differences in riverbed slopes, the HYP_{POT} index shows an important difference between the two selected stretches. It is also worth noting that the obtained values are an order of magnitude lower than the potential of mountain streams given by Wondzell (2011), and at the same time higher than that of the Moszczenica in its middle course (Ziułkiewicz 2022).

VHG measurements carried out in particular seasons showed two main circumstances:

1) The existence of two zones of strong upwelling in the erosive stretch of the riverbed – one in the vicinity of the Ru-2 source, the other in this part of the channel where the erosive stretch turns into an accumulative one. Between winter and summer observations in the upper zone, the upwelling weakened and the places where it occurred dispersed. The second zone was successively moving up the valley, also losing strength.
2) More cases of downwelling were found in the accumulative stretch than in the erosive stretch. The downwelling was strongest in June 2021 and just a little weaker in December 2020. However, in March 2021, this phenomenon was significantly reduced so that, on average, there was a change in the direction of water exchange between the riverbed and the HZ (Table 3).

In general, the strength and direction of VHG obtained with a denser network of measurement points in December 2020 (Fig. 4A) does not indicate that the course of the Malina channel was the main factor determining the exchange conditions between the watercourse and its HZ. At meanders (especially well-developed ones in the erosive stretch), downwelling zones were not concentrated upstream of them, and no upwelling zones were found downstream of them. What is visible, however, is the existence of relatively short zones of downwelling or upwelling in the bottom of the watercourse, ranging in length between several meters and about 40 m, wherein longer ones were better marked in the accumulative stretch.

Hydrochemical data in terms of basic physicochemical parameters and concentrations of mineral forms of nutrients makes it possible to complete the observation of the size and direction of VHG in the erosive and accumulative stretch. They indicate that with a significant difference in the value of the HYP_{POT} index, conditions favour upwelling in the upper part of the riverbed and downwelling in the lower part (Table 1). In simple terms (which can be treated as a working hypothesis), this means that, in the HZ of the erosive stretch, the dominant mixing component are groundwaters from aquifers drained by the Malina, while in the lower, accumulative stretch, river waters have a significant share in the hyporheic mixture. Therefore, the waters from the HZ should be expected to be hydrochemically similar to spring waters (Ru-2) in the erosive stretch (these latter being representative of groundwaters). By contrast, they should be more similar to the Malina river waters (Ma-3, Ma-4) in the lower, accumulative part. In the winter season (Fig. 6A), hyporheic waters showed a clear similarity to river waters: the river water of the erosive stretch (Ma-1 and Ma-2) was similar to spring waters (Ru-2) and to HZ waters at the strong upwelling close to the spring niche. In the middle course (Ma-3), the stream waters were similar to the HZ waters in the strongest upwellings found in the whole studied river section. The same similarity, though weaker (weaker VHG values) was found in the lower course (Ma-4). The size of VHG and the layout of hyporheic water sampling points indicate that the HZ may have been one of the most important determinants of the hydrochemical properties of the river waters in December 2020. In March 2021 (Fig. 6B), the waters of the Malina, with the effective impact of other sources of supply, showed hydrochemical independence from the HZ. In the next season, the Malina waters maintained their hydrochemical separation from the HZ and spring waters (Fig. 6C). Individual cases of strong similarity hyporheic waters with the river waters in spring and summer may indicate the local influence of the Malina on its HZ. Three of them are located in accumulative stretch.

Another point is worth attention: the scale of hydrochemical anisotropy of the HZ observed along the course of the Malina river. The phenomenon of anisotropy has been described by, for example, Zarnetske et al. (2010), Zimmer and Lautz (2014), Boano et al. (2014), Ziułkiewicz (2022), and Krogulec et al. (2024). It is particularly visible in the lower part of the erosive stretch, where in December 2020 between the neighbouring sampling points of hyporheic waters (m-38/m-40 and m-17/m-18 – Fig. 3A), SEC changed by 750 µS/cm and 444 µS/cm, respectively. In March 2021, a large difference in $N\text{-}NO_3$ concentrations was recorded between neighbouring HZ sampling points in m-17 and m-18, where it reached 9.7 mg/dm^3, and in m-29/m-30, where it was 5 mg/dm^3. In June 2021, in the lower part of the accumulative stretch, a 5 mg/dm^3 difference in $N\text{-}NH_4$ concentrations was found between m-2, m-3 and m-4. At the same time, in many parts of the HZ no ammonium and nitrate nitrogen were found, which indicates special redox conditions prevailing there. Important in this respect is the carbon content in alluvia and the efficiency of downwelling of oxygenated river waters (Harvey et al. 2013). Analyses showed that the content of C_{org} in the upper (up to 25 cm) layer of the riverbed bottom formations range from 0.03 to 0.66% and generally it is on average more in the erosive stretch than in the accumulative one (Table 2).

Changes in the concentrations of mineral forms of nitrogen between downwelling and upwelling sites indicate the possibility of simultaneous denitrification and nitrification, which may be related in various ways to the presence of microhabitats of organisms capable of performing both reactions (Vymazal & Kröpfelová 2008). The observations showed that, in the HZ on the accumulative stretch, nitrate nitrogen disappears and ammonium nitrogen is released, which in fact occurs in the hyporheic zones of rivers (Hill et al. 1998). Gordon et al. (2013) and Hester et al. (2016) note that, although the hyporheic zone's ability to reduce nitrate loads in individual stream stretches may be small, the cumulative nitrate removal capacity over longer stretches or stream networks can be significant under favourable environmental conditions. In the Malina, with a large scale of catchment exposure to urban contaminants, this is unfortunately not the case. The increase in the load of N-NO_3 in the riverbed in each season was the greater, the stronger the average VHG for the entire stretch of the stream under study, i.e. the largest loads flowed down the river in upwelling conditions, and the smallest ones in downwelling conditions. When upwelling dominated in a given season, the loads of ammonium nitrogen and orthophosphate phosphorus rose in the accumulative stretch. On the basis of these differences, the complex geochemical nature of both stretches can be revealed:

1) In the erosive stretch, with a potentially more extensive HZ, the oxygenated river waters have better conditions for penetration into riverbed bottom sediments containing a larger amount of organic carbon, which should be conducive to nitrification. However, there are few downwelling sites and they have a low VHG, so the released of nitrates from the HZ to the stream should rather be associated with the inflow of pollutants from the Malina groundwater basin. However, as reported by Zarnetske et al. (2011), it should be taken into account that anaerobic micro-zones with redox potentials reaching the conditions of sulphate respiration occur even in oxygenated sediments, where nitrates may also be released as a result of coupled nitrification-denitrification reactions (Triska et al. 1993b).
2) In the accumulative stretch, with a weaker potential for HZ development, downwelling can be associated with increased loads of N-NH_4 and P-PO_4, nutrients released in the reducing environment due to mineralisation of organic matter. In addition, phosphates may be released by reductive dissolution of iron-bound phosphorus or bedrock weathering (Vymazal & Kröpfelová 2008). Lewandowski and Nützmann (2010) note that phosphates can be released in the HZ only if they have been previously collected, absorbed or delivered there in the form of solid particles by sedimentation or filtration. Earlier studies of the Malina river waters (Gajda 2021) showed that PO_4^{3-} concentrations are associated with changes in total suspended solids, which, under the stream's prevailing transport conditions, has better sedimentation possibilities in the accumulative stretch. The nature of the Malina catchment's development should be borne in mind (Fig. 1), as Hancock (2002) mentions that significant anthropogenic impacts on the HZ include increased transport of suspended solids from an urbanised catchment, which results in the bottom of rivers being sealed, thereby creating anoxic conditions in the HZ. Another effect of the suburban location of the Malina catchment may be the inflow of nutrients to the HZ with underground waters polluted outside the valley.

Calculated filtration times of river water through HZ in two scenarios (Table 3) give a span from less than 18 hours to 3 days. In that time, in the winter season, nitrates were completely removed from the water. In summer, with a longer time of water flowing in the HZ, the efficiency of removing nitrate nitrogen was clearly weaker, and the concentration increase of ammonium nitrogen was as low as in December 2020. The obtained times and scale of N-NO_3 concentration changes in our calculations are comparable to the results of Zarneske et al. (2011), in whose study the concentration was reduced from 0.54 to 0.03 mg/dm^3 in one day. Denitrification is already possible in the redox potential since +200/+250 mV, while the ammonification of nitrates below –100 mV (Vymazal & Kröpfelová 2008). The redox potential in the hyporheic waters of the Malina in relation to N-NH_4 and N-NO_3 concentrations shows that the conditions in the riverbed sediments are complex and favour both reactions (Fig. 7). It should be added that the pH reaction of hyporheic water was optimal for ammonification, nitrification or denitrification, i.e. pH 6.0–8.5 (Vymazal & Kröpfelová 2008). Organic carbon content in the riverbed bottom sediments should be considered small, so according to Tiedje et al. (1982) denitrification will be a preferred process of atrophy of nitrates, rather than NO_2^- and NO_3^- dissimilation to ammonia.

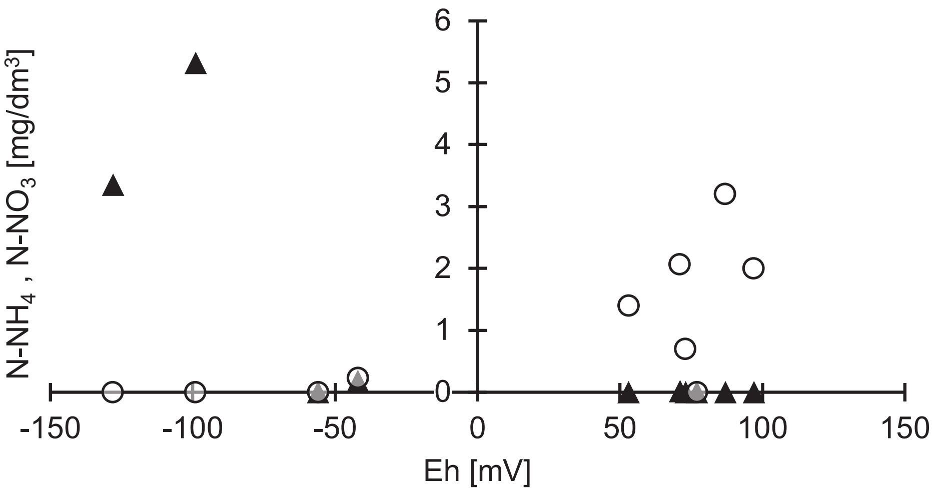

Fig. 7. *Concentrations of nitrogen mineral forms in depending on redox potential of hyporheic waters in June 2021:* ▲ *– N-NH$_4$,* ○ *– N-NO$_3$*

Moreover, according to Koike and Hattori (1978), dissimilation can occur in systems that are anaerobic for a long time, while the bottom sediments of the Malina are subjected to variable penetration by oxygenated river waters and show the lability of redox conditions (Fig. 7), which confirms the hypothesis of denitrification as a fundamental process for removing nitrates. Studies by Grulke and Ziułkiewicz (2022) indicate that the waters of the Malina section under study are characterised by very good oxygen conditions. It was found that the concentrations of oxygen dissolved in the river water between the Rudunki II reservoir and the forest ponds gradually increased and in the accumulative stretch were in the range of 8.4–11.8 mg/dm^3 (mean: 9.9 mg/dm^3 for n = 16) at water temperatures in the range of 4.4–13.5°C. It can therefore be assumed that very-well-oxygenated water penetrated the HZ.

CONCLUSIONS

The Malina river sediments proved to be well permeable, with the hyporheic exchange potential being an order of magnitude higher for the erosive stretch than the accumulative stretch. The results of the hydraulic gradient measurements did not show the expected pattern of water exchange between the river and the HZ according to conceptual model (Biksley & Gross 2001, Gooseff 2010): instead, we found upwelling predominated in the gorge section and downwelling in the pool part of valley. Another element differentiating the HZ environment was the content of organic carbon, which, with the distribution of the hydraulic gradient changing in time and space and the functioning of the zones of preferred groundwater inflow, created an anisotropic HZ hydrochemical environment in the bottom sediments of the Malina. The strongest evidence of its impact on the stream through upwelling zones was collected in winter. In the spring, the hydrochemical connection was the weakest and limited to single places where surface waters could appear in the HZ as a result of high-water damming on jams formed in the Malina riverbed. In the summer, river waters maintained their hydrochemical distinctness from HZ and spring waters, although circumstances were locally identified that indicated the presence of poorly chemically transformed river waters in the HZ.

The research proved that the increase in the nutrients load flow down the Malina was the highest at the time of the strongest positive VHG, i.e. in the winter, when hydrochemical connections between river waters and hyporheic waters are strongest. It turned out that in all three seasons there was an increase in nutrient loads in the erosive stretch, while reductions occurred in the accumulative stretch, especially in spring. In the case of N-NO_3, the increase in its load was the greater, the stronger the average VGH was for the whole studied Malina section, i.e. that the amount of nitrate nitrogen flowing down the river was largest in upwelling conditions and least in downwelling conditions.

Calculations of the time of the river water filtration through the HZ sections in as compared to the nutrient concentrations proved that changes in such concentrations in time periods ranging from less than one day to three days were in the same direction but clearly greater in December 2020 than in June 2021. Off-the-scale poor quality waters in terms of nitrate nitrogen became off-the-scale poor quality in terms of ammonium nitrogen concentration. The increase in the concentration of orthophosphate phosphorus also did not change the off-the-scale chemical status of the waters before and after the "trip" of the river waters through the HZ.

In the scope of the above results, it seems that winter is a very important period in shaping the interaction of river waters with the underlying hyporheic zone, in which the causal side of the relationship should be associated with the subchannel environment, and the effects are observed in the river.

The nutrients delivered to the Malina river in the erosive stretch are related to the inflow of nutrient-rich groundwater from the urbanised catchment. The pollutants transported down by the stream are then delivered to the HZ in the accumulative stretch, where nitrates are denitrified and phosphates are deposited with the suspension. Ammonium nitrogen, in turn, is introduced into the watercourse from the HZ as a result of either the process of the ammonification of organic matter deposited in sediments or inflow with polluted groundwater. A similarly complex genesis is shown by P-PO_4, which can be mobilised from sediments in the HZ as a result of the redox conditions prevailing there or delivered from the underground catchment.

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