Karst regions are characterized, among other features, by a specific type of hydrology, displaying a relatively high infiltration rate, a variable flow rate, the concentration of water flow (e.g., along fissures), long-distance underground flow, etc. (Ford and Williams, 2007). These features influence not only the mode of discharge of a karst area in its reaction to rainfall/snow-melt events, but also the hydrochemistry and transport of substances via surface water and groundwater. Both reaction to water input and transportation in water, for example as dissolved substances and as suspended particles, are much faster in karst deposits than in a porous aquifer.

The complexity of karst hydrological systems demands unusual methodology for the tracking of water flow paths and their intensity. The methods most often applied include the study of the rate of water discharge (e.g., at a drip point or a karst spring) and its relationship to the amount of precipitation. In this case, the speed of water wave is estimated. Another way to track water flow in a karst system is by using fluorescent dyes, for example uranine or rhodamine (Goldscheider et al., 2008), and measuring the time of dye flow to the discharge point. In this case, the time of transport of dye molecules is measured. Both groups of methods demand long-term monitoring or tracking water transport only along with one or more, previously selected flow paths.

An alternative for studies of water flow is methods based on natural elemental or isotopic markers. These methods require two main assumptions: 1) the water from a different area of alimentation has a different elemental/isotopic signature; and 2) concentration/activity of a particular element/isotope is above the detection limit of the measuring method used. Tritium, a radioactive isotope of hydrogen, was the most widely used during the last several decades as an isotopic tracer in hydrogeological studies (Carlston, 1964; Solomon and Cook, 2000; Ford and Williams, 2007; Beyer et al., 2014). The main source of tritium in the atmosphere were bomb tests, carried out in the 1960s. After several decades, this pool of tritium almost completely disappeared, owing to the relatively short half-life ($T_{1/2} \sim 12$ yr.) of this isotope. Although tritium is also naturally produced in the upper part of the atmosphere, its low activity limits...
using this radioisotope as a natural tracer. Despite that fact, the application of tritium in the Niedźwiedzia Cave system allows recognition of at least two sources of water discharge in karst springs and estimation of its average age as ~4 yr (Gąsiorowski et al., 2015). However, in that specific case, studies on tritium activity have not allowed determination of the water alimentation area.

The Niedźwiedzia Cave system developed in a relatively small lens of crystalline limestone, surrounded by metamorphic rocks. The metamorphic rocks in the area have elevated uranium content, which was formerly exploited in the mine located 1.5 km to the north of the cave entrance (Sobień and Nawrocki, 2010). On the other hand, the crystalline limestone is characterized by low uranium content, which creates difficulties in the application of the U-Th method for dating secondary carbonates, deposited inside the cave (Hercman et al., 1995; Lechleitner et al., 2016).

In nature, the most abundant uranium isotope is 238U (99.28%), and subsequently 235U (0.72%) and 234U (0.005%; Markich, 2002). Under reducing conditions, uranium occurs naturally in the stable form and in the tetravalent state (Bourdon et al., 2003). It is a component of various minerals, for example, monazites and allanites, which occur in different rock type. As a result of the weathering of such rocks, uranium isotopes become highly mobile and able to migrate in the environment. Under oxidizing conditions, uranium creates metal oxide ions and free metal ions, that is, UO₂²⁺ (uranium oxidation state [VI]), UO₂⁻ (U[V]) and U⁴⁺ (U[IV]), respectively (Markich, 2002). In aquatic systems, uranium occurs mostly in the hexavalent form and creates soluble complexes with phosphate and carbonate (in near to neutral pH conditions), fluoroide and sulphates (at a lower pH) and humic substances, such as humate (Markich, 2002; Bourdon et al., 2003). The availability of complexing ions, their concentrations and pH conditions strongly influence the abundance of the uranium species (Gascoyne, 1992).

One of the products of 238U decay (a uranium-radium series) is polonium 210Po, the radioactive decay half-life of which is 138.4 d (Be et al., 2010). Accordingly, the abundance of 210Po in rocks depends, to some extent, on the uranium content and its decay products in the environment. However, the amount of polonium originating from the direct disintegration of uranium can decrease with radon emanations and increase with the deposition of lead 210Pb and polonium 210Po from the atmosphere. Furthermore, it also can be supplied by anthropogenic inputs (e.g., uranium mining; Ferrari et al., 2017). The occurrence of 210Po in the aquatic system is determined by precipitation in sulphides, adsorption onto the surfaces of clay particles and biovolatilization (Carvalho et al., 2017). Polonium is highly insoluble and has several oxidation states, ([II]-, [II⁺], [IV⁺], and [VI⁺]). In the tetravalent state, it is insoluble and stable in oxic conditions; nevertheless, it also can form hydroxides. Generally, polonium in groundwater is bound to the intermediate and small particle fraction, for example iron and manganese hydroxides and humic substances (Vaaramaa et al., 2003). In addition, low polonium values in aquatic systems may be related to the fact that it can be precipitated under anoxic conditions (Carvalho et al., 2017).

The major aim of this study was to detect the alimentation area for water discharging in the karst system of Niedźwiedzia Cave. The authors hypothesized that water flowing through metamorphic/crystalline rocks has a higher uranium content than water flowing only through marble. On the basis of this assumption, the authors hope to distinguish between water flowing outside of the marble outcrop area (lateral flow and deep circulation; high uranium content) from meteoric water infiltrating only through crystalline limestones (low uranium content). In addition, polonium, being much less soluble in karst waters, was treated as an indicator of autochthonous water, infiltrating through the soil cover and containing a relatively large amount of small size (<0.45 mm) particles.

**MATERIAL AND METHODS**

**Study site**

The Niedźwiedzia Cave system is located in the eastern part of the Sudety Mountains (Poland), in the valley of the Kleśnica Creek, a tributary of the Biała Łudecka River. The cave system is developed in a small lens of marbles (crystalline limestones), surrounded by metamorphic schists and paragneisses of the Stronie Formation (Don et al., 2003). The main trend of the corridors of the cave is parallel to the longest axis of the limestone lens (Fig. 1). Besides the main direction, several corridors are developed at three levels of the cave system and they probably functioned as additional access points for water coming into/out of the cave. The cave is composed of three horizontal levels of passages, joined by means of several shafts (Bieroński et al., 2009). Nowadays, the system is fed with water of the Kleśnica Creek entering the cave by a system of ponors or via fissures cutting the marble lens. This water is present mainly in the lower, active level of the system. The second source of water is atmospheric water, infiltrating from the surface directly above the cave, and this water feeds drip points in the middle and upper levels (Gąsiorowski et al., 2015). The system is drained mainly by karst springs located at the level of the Kleśnica Creek, below the entrance pavilion to the cave. Some amount of water is transported along the contact zone of the marbles and the schists to the south (to the Morava Valley in the Czech Republic) and to the north, along the Kleśnica Valley. Dye studies also indicate that there are some unknown avenues of discharge (Ciężkowski et al., 2009).

**Sampling**

The water samples were collected at several sites in the Kleśnica Valley (precipitation, the waters of streams and karst springs) and inside the cave (Fig. 1), on a monthly basis for 2 years. The sites outside of the cave were selected to characterize the water of the Kleśnica Creek above the cave, in the ponor zone, in the karst stream zone and below the known parts of the cave system. Also, water samples from some of the tributaries of the Kleśnica Creek.
were collected. Precipitation water was collected from the roof of the entrance pavilion to the tourist route. Inside the cave, water was sampled from drips off the stalactites (one point at the middle level and two points at the lower level), from sinter pools (one pool at the middle level and one at the lower level) and from the underground part of the Klesnica Creek. Water was collected in 10- or 22-litre polypropylene containers. Immediately after sampling, the water was acidified with 50 mL of 65% HNO$_3$ to avoid precipitation of radionuclides on the container walls, and spiked with a mixture of $^{208}$Po + $^{209}$Po + $^{232}$U dissolved in nitric acid to control the chemical recovery of the isotopes studied. The amount of spiking mixture added was controlled by means of an analytical balance with 0.01 mg readability.

**Radionuclide measurements**

Sequential separation was used to recover the radionuclides from the water samples. This procedure is based on the methodology proposed by Benedik et al. (2009). The polonium and uranium isotopes were extracted from the samples by utilizing their co-precipitation with iron hydroxide, using ammonia and iron chloride (Narita et al., 1989). The solution above the precipitant was decanted and the precipitant was centrifuged at 4,000 rpm over 10 min. After that, the residue was dissolved in nitric acid and oxidized with hydrogen peroxide until its colour disappeared. Next, the solution was evaporated and the residue was dissolved in hydrochloric acid. The next step in the procedure was the reduction of Fe$^{3+}$ to Fe$^{2+}$, using hydroxylamine hydrochloride (Flynn, 1968; Ham et al., 1997) and ascorbic acid (Blanchard, 1966; Martin and Blanchard, 1969). Subsequently, spontaneous electrodeposition of polonium on silver discs was performed in an environment of 0.5 M hydrochloric acid (Matthews et al., 2007). Chemical recovery of the polonium ranged from 70–90%. In order to separate the uranium isotopes, the solution remaining after polonium deposition was treated according to the standard procedure of Ivanovich and Harmon (1992). Uranium was separated out of the solution on chromatographic columns (Horwitz et al., 1993), using a DOWEX 1x8 resin and electrodeposited on stainless steel discs. The typical chemical recovery for uranium was 10–50%. Finally, the activity of the $^{210}$Po and U isotopes was measured, using the Octete (Ortec®) alpha particle spectrometer (detector active area 1,200 mm$^2$) at the Uranium Series Laboratory of the Institute of Geological Sciences, Polish Academy of Sciences in Warsaw. The lower detection limit for counting over 600,000 s was 0.07 mBq dm$^{-3}$ for polonium and 0.02 mBq dm$^{-3}$ for the uranium isotopes. The results for polonium and uranium activities were reported with 2σ uncertainties.
RESULTS

Polonium activity

The polonium activity in water samples varied with time (Fig. 2A) and between sites (Fig. 2B). Generally, surface water shows a greater variability of $^{210}$Po activity, compared to water inside the cave and the only exception is the water in the sinter pool at the middle level of the cave (site JN-7). The lowest activity, below the detection limit ($<0.07$ mBq dm$^{-3}$), was recorded in a sample from an artesian spring in the Kleśnica Valley (site JN-3). Also, other samples from that site give very low activities (below 1.0 mBq dm$^{-3}$), except for a sample taken two months after a heavy flood event. The greatest activity of polonium (up to $65.9 \pm 5.8$ mBq dm$^{-3}$) was recorded in a sample from sinter pool at the middle level of the cave (site JN-7). In general, higher mean activities were recorded in the samples from the cave and particularly at the lower cave level, the polonium activity value was stable for a year. Although surface water is relatively depleted in polonium, the exception is Kleśnica Creek water (sites JN-1 and JN-5), sampled during summer months (high precipitation and high discharge period), especially during the flood event of July 22, 2011 (Fig. 2A). The activity recorded at this time was $44.2 \pm 2.5$ mBq dm$^{-3}$ and $43.2 \pm 2.2$ mBq dm$^{-3}$ for sites JN-1 and JN-5, respectively.

![Fig. 2. Polonium $^{210}$Po activity in water samples. A. Changes in activity of polonium $^{210}$Po in time in water samples from the Niedźwiedzia Cave karst system; B. Activity of polonium $^{210}$Po in water samples from the Niedźwiedzia Cave system. Site codes as in Figure 1. Asterisks indicate outliers not included in the calculation of mean and median values.](image-url)
Uranium activity and $^{234}$U/$^{238}$U activity ratio

Uranium activity in surface water of the Kleśnica Valley increased downstream (Fig. 3), namely the highest mean values of activity, but also the highest variability in time, was recorded below the marble outcrop (site JN-5). At this site, the uranium activity varied from below the minimum detectable activity (<0.02 mBq L$^{-1}$) up to 19.24 ± 0.18 and 14.86 ± 0.16 mBq L$^{-1}$ for $^{234}$U and $^{238}$U, respectively. The highest values, as in the case of polonium, were measured during the flood event of July 2011. Also, the site above the ponor zone (JN-1) exhibited relatively high activities of both uranium isotopes during the flood event but was low in other periods. The lowest values of $^{234}$U and $^{238}$U activity, below the detection limits, were measured for rain samples. Also, sites JN-7 and JN-8 at the middle level of the cave system were characterized by low uranium content. The lowest variability in uranium activity was in underground stream water (JN-14) and in a karst spring (JN-2).

The activity ratio of uranium isotopes ($^{234}$U/$^{238}$U) varied from 0.7 ± 0.1 in a sinter pool at the lower cave level (JN-12) to 4.12 ± 0.16 at drip site at the lower cave level (site JN-10; Fig. 4), and the median and mean values were 1.4 and 1.6, respectively. The ratio was relatively stable in Kleśnica Creek water, where it varied between 1.17 ± 0.04 and 1.76 ± 0.24. On the other hand, the greatest variation in $^{234}$U/$^{238}$U ratio was calculated for a drip site at the middle and lower level of the cave. There, the ratio ranged from 0.8 ± 0.1 to 2.47 ± 0.13 for site JN-8 (middle level) and from 1.15 ± 0.03 to 4.1 ± 0.2 for site JN-10 (lower level).

**DISCUSSION**

Polonium is generally highly insoluble in karst water and can be transported mainly as ions adsorbed to suspended particles. This explains why maxima in surface waters were reported during high-discharge (flood) events, related to the intensive erosion and transport of detritus. The amount of suspended material in dripping water inside the cave is less and not so variable (Simon et al., 2013). Polonium reflects this, as it is clearly more stable during the year in water inside the cave. The only exception was a sinter pool at the middle level of the cave (JN-7). There, clearly elevated activities were recorded during the late spring/summer period (Fig. 2A). The most probable explanation of this phenomenon is a higher concentration of radon $^{222}$Rn in the air of the cave during the warmer period of the year (Przylibski and Piasecki, 1998), caused by poor ventilation of the cave. Radon, a parent isotope of polonium $^{210}$Po, usually is considered to be a major source of polonium inside the cave (Cigna, 2005; Field, 2007). This effect disappears during the winter, when there is an inflow of warm air into the cave from the outside by way of a system of fissures. The other explanation for high $^{210}$Po activity at site JN-7 is the contamination with polonium, transported by visitors in the mud fraction and then washed into the sinter pool from the tourist path. The fact that summer is the high season for tourist activity in the cave could support this thesis. The polonium input from atmospheric deposition seems to be negligible in these cases.

Compared to other areas in Poland, the Kleśnica Valley water has significantly higher activities of $^{210}$Po. For example the maximal value recorded in the Kleśnica Creek water is two orders of magnitude higher than that in deep-intake water in the northern part of Poland (Skwarzec et al., 2001) or in water from the Oligocene sand aquifer of Central Poland (Sekudewicz and Gaśiorowski, 2019). On the other hand, the reported values are still very low, compared to some regions with crystalline rocks in Finland and the U.S., where the measured $^{210}$Po activities exceeded 13,000 and 16,000 mBq L$^{-1}$, respectively (Seiler, 2016). The internal production of polonium from U-series isotopes present in rocks in the vicinity of the cave seems to have a low effect on the total budget of polonium.

As polonium concentration is highly variable in surface water and relatively stable in karst water and groundwater, it potentially could be used to track increasing input of surface water into an aquifer. In the karst system analysed, the authors recorded an admixture of surface water in water from an artesian spring in the Kleśnica Valley (site JN-3). There, the clear increase in polonium was recorded ~2 months after the peak in activity of the water of the creek, related to
the flood event. This observation had been confirmed previously on the basis of tritium activity (Gąsiorowski et al., 2015), which was similar in artesian water and rainfall.

The uranium mean activity and activity variability inside the cave were clearly lower than in the surface water. This can be related to the origin of the water dripping at the sites studied and the water circulation routes. Generally, the only source of water in the inactive passages of the cave, meaning the upper and middle levels of the cave system, is the infiltration of rain and melting snow from the area directly above the cave passages. Infiltration through the thin soil and regolith layer (thickness ~30–50 cm) and carbonate rocks is relatively slow and takes ~6 months at the middle cave level (Gąsiorowski et al., 2015). This period seems to be not enough for the leaching of a significant amount of uranium from the rocks. Furthermore, marbles at Kletno are characterized by low uranium concentrations, which was the reason for difficulties in the U-series method of dating of speleothems at Niedźwiedzia Cave (Hercman et al., 1995; Lechleitner et al., 2016). This was confirmed by means of field measurements of marbles in the cave passages, where the mean total gamma activity was only 34.5 ± 0.5 dpm (unpublished data). Accordingly, in the lower, active level of the cave system, the uranium activity in dripping water is also low, with the exception of one drip point with a high mean discharge (site JN-10). There, the higher activity might be related to the longer circulation time of the water, up to ~1 yr (Gąsiorowski et al., 2015), the admixture with water originating outside the marble area, or the relatively high uranium content, originating from the soil/regolith layer. The latter factor is the most probable, since there is also high enrichment in 234U (Fig. 4).

The water of the Kleśnica Stream is a mixture of “allo-
genic” water, originating in the part of the catchment located above the marble area and water “autogenic” for the karst system. The alloogenic water is characterized by a relatively higher uranium concentration. The uranium in this water originated in the metamorphic rock complex, surrounding the marble outcrop (Fig. 1). In these rocks, uranium occurs both in a dispersed form and as uranium-bearing minerals, concentrated in polymetallic and fluorite-quartz veins (Banaś, 1965). The biggest concentration of uranium ores is located some 1.5 km to the north of the cave and was exploited commercially in the 1950s. On the other hand, the uranium mine itself has only a limited impact on the concentration of U-series isotopes in surface water (Chruściel et al., 1996). Most of the Kleśnica tributaries have springs in significant parts of the catchment area outside the marble outcrop and therefore can leach uranium from the metamorphic rocks. This is confirmed by the high variability of uranium concentrations in surface waters and its dependence on water discharge; the higher activities were measured during flood events.

234U/238U activity ratios of the Kleśnica Creek water are in the range typical for river water. In natural freshwater, the activity ratio of 234U to 238U exceeds 1.0, owing to the alpha-particle recoil effect and the preferential mobilization of 234U to groundwater from rocks and soil (Petit et al., 1985). Chabaux et al. (2008) reported that typical river water has a 234U/238U activity ratio of 1.0–1.4. Higher values, up to 9.02 (Boryło and Skwarzec 2014), could be the effect of supply from groundwater. In fact, at the site below the marble outcrop, where the stream collected also water from the karst springs and artesian water (site JN-3), the 234U/238U

![Figure 4](image-url)  
**Fig. 4.** Uranium 238U activity vs. uranium (234U/238U) activity ratio. Site codes as in Figure 1.
activity ratio is higher, up to 1.76 ± 0.24. The same value was reported for site JN-4, one of the Kleśnica tributaries, indicating also the input of groundwater into this stream. If the $^{234}\text{U}/^{238}\text{U}$ activity ratio would be applied as a measure of the length of the water circulation route in the massif (especially through soil and the epikarst zone), the water was collected from the drip point with a relatively high discharge at the lower cave level (site JN-10). Moreover, discharge at these sites is not strongly correlated with rain intensity and indicates supply from water percolating longer in the epikarst zone. This is in general agreement with the drip intensity and tritium activity at these sites (Gasiorowski et al., 2015). The $^{234}\text{U}/^{238}\text{U}$ activity ratio of close to unity indicates young, meteoric water in limited contact with the rock/soil matrix and non-selective leaching of both uranium isotopes. This occurs at sites with a high discharge/dripping rate, but only during high precipitation/flood events (e.g., at site JN-8). During low-discharge events (e.g., in winter), the $^{234}\text{U}/^{238}\text{U}$ activity ratio, even at such a site, can be above 1.4. The exceptionally low $^{234}\text{U}/^{238}\text{U}$ activity ratio (below 1.0) was measured for samples from sinter pools during dry periods. A possible explanation could be the re-dissolution of calcite formerly precipitated in the pools, which has a greater amount of $^{238}\text{U}$. Another possibility is leaching of the weathered rocks of the regolith layer, previously depleted in $^{234}\text{U}$ (Andersen et al., 2009).

**CONCLUSIONS**

Polonium in the samples studied originated mainly from the detrital contamination of water and, to a lesser extent, was leached from aquifer rocks. Accordingly, it may be used as an indicator of the extent of water circulation in the massif. Water input from karst rocks has no effect on the uranium concentration in the Kleśnica Creek. The concentration of uranium increased downstream because of the gradual leaching of radiogenic uranium from aquifer rocks. Accordingly, it may be used as an indicator of the extent of water circulation in the massif. Water input from karst rocks has no effect on the uranium concentration in the Kleśnica Creek.

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