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DRIP RATE AND TRITIUM ACTIVITY IN THE NIEDŹWIEDZIA CAVE SYSTEM (POLAND) AS A TOOL FOR TRACKING WATER CIRCULATION PATHS AND TIME IN KARSTIC SYSTEMS

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Abstract: The Niedźwiedzia Cave system is composed of 3 horizontal levels of passages and chambers. Changes in the drip rate of water from the upper level stalactites correlate well with changes in precipitation intensity. The transition time between the surface and the upper level of the cave was estimated to 14 days. Drip sites in the middle and lower levels of the cave exhibited two types of recharge: some did not correlate with precipitation intensity, whereas others correlated well with rain events. The transition times for the latter sites were estimated to be greater than 6 months. This estimate was confirmed by the calculation of the transition time based on tritium activity. The oldest water in the entire karst system was observed in a karst spring. The mean tritium age for this water during winter was estimated to be 3.9 ± 0.6 yr. More precise calculations of the tritium age of karst water require longer precipitation activity datasets.

Keywords: karst hydrology, drip rate, speleothems, tritium, transitional time.

1. INTRODUCTION

Tracking water circulation paths is one of the most important issues in karst studies. The complex hydrology of karst areas, with significant amounts of water transported by underground flows, makes this issue important at the regional scale.

Precipitation infiltrates through soil and rock and discharges into caves in the form of drip water. The infiltration behaviour of water demonstrates high variety, even among nearby drip points (Smart and Friedrich, 1986). The individual properties of each drip site are related to complex flow paths. The flow paths usually vary through time due to typical seasonal changes in precipitation intensity. Different drip sites react differently to precipitation events. Studies of these responses can help estimate the transition time (infiltration time) of precipitation. Measuring the time associated with a response to a precipitation event is one of the simplest natural tracers of infiltration time and paths (Ford and Williams, 2007). Other tracers involve the concentration (or activity) of natural elements or isotopes transported by karst water. For example, tritium (^3H) is an isotope that has been previously used in karst studies. Tritium is a natural radioactive isotope of hydrogen formed in the stratosphere as a result of nitrogen atoms interacting with the fast neutrons of cosmic rays (Craig and Lal, 1961). Subsequently, tritium is seasonally injected to the troposphere, mainly during winter and early spring. Tritium has been widely used in studies of karst hydrology to calculate transitional times, to assess contamination of aquifers with meteoric water and as an isotopic tracer (Price *et al.*, 2003; Ozyurt and Bayari, 2005; Kluge *et al.*, 2010). Because it is integral part of water, tritium is a much better tool for estimating the transport of water, flow rate and circulation

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paths than other markers, e.g., dyes. The natural activity of tritium in the atmosphere was 2–8 tritium units (1 TU is equal 1 ^{3}H atom per 10^{18} atoms of hydrogen) before 1952 (Clark and Fritz, 1997). In the years following 1952, tritium activity increased until 1963, when tritium levels peaked. This artificial increase was caused by nuclear bomb tests in the atmosphere. After 1963, the global tritium content has systematically decreased due to the limitation of nuclear tests and the relatively short half-life of this isotope (12.32 ± 0.02 yr; Lucas and Unterweger, 2000). Recently, the tritium activity of precipitation and surface waters has decreased to near-natural values of 5–10 TU (Theodorsson, 1999). This fact strongly limits the use of tritium as a tool for water dating. Such studies require new, sensitive, low-background methods of detection.

Discovered in 1967, the Niedźwiedzia Cave system (Sudetes, Poland) has been studied for several decades. Recent studies have focused primarily on morphology, sediment characteristics and description of Late Pleistocene fauna e.g., the significant quantity of cave bear remains (Bieroński *et al.*, 2009). The cave system is hydrologically complex: it is fed by the infiltration of precipitation, lateral inflow of stream water and deep-circulation water and is partially drained by a system of karst springs in the Kleśnica valley and the Morava valley (Czech Republic). In spite of intensive studies, the circulation paths are not fully understood (Ciężkowski *et al.*, 2009).

The aim of this study was to establish relationships between the intensity of precipitation and the drip rate of selected drip sites in every level of the cave system. These data, supported by the tritium content in karst water, were used to estimate the transition (infiltration) time to each level of the cave and to the better understanding of the water circulation pattern in the Niedźwiedzia cave system. We present the results of drip rate measurements and tritium content results from precipitation, surface water, underground steams and drip water.

2. STUDY SITE AND MEASUREMENT STATIONS

Niedźwiedzia Cave (N 50°14,068', E 16°50,558'; **Fig. 1**) was described in detail by Bieroński *et al.* (2009), and only the essential facts are discussed here. The cave, with a known passage length of over 4000 m, is the biggest cave system in the Polish part of the Sudety Mountains. The two artificial entrances are at elevations of 800 and 807 m a.s.l., *i.e.*, 10 and 15 m, respectively, above the actual bottom of the Kleśnica valley. The cave was formed in a marble unit among mica schist and gneisses with Ediacaran-Cambrian ages. The system has 3 levels of passages and chambers connected by several fissures and chimneys. The upper level is preserved only in a small fragment above the Pałacowa Chamber in the middle level (**Fig. 1**). The middle level of the system is a show cave with over 80 000 visitors per year. This part of the cave was adapted for touristic traffic, e.g., artificial paths made of concrete were built along the tourist route. The adaptations changed the water conditions (e.g., accelerating discharge from sinter pools) in several places in the middle level. The lower level of the system is an active part of the cave with several underground streams supplied mostly by ponors located in the Kleśnica stream bottom.

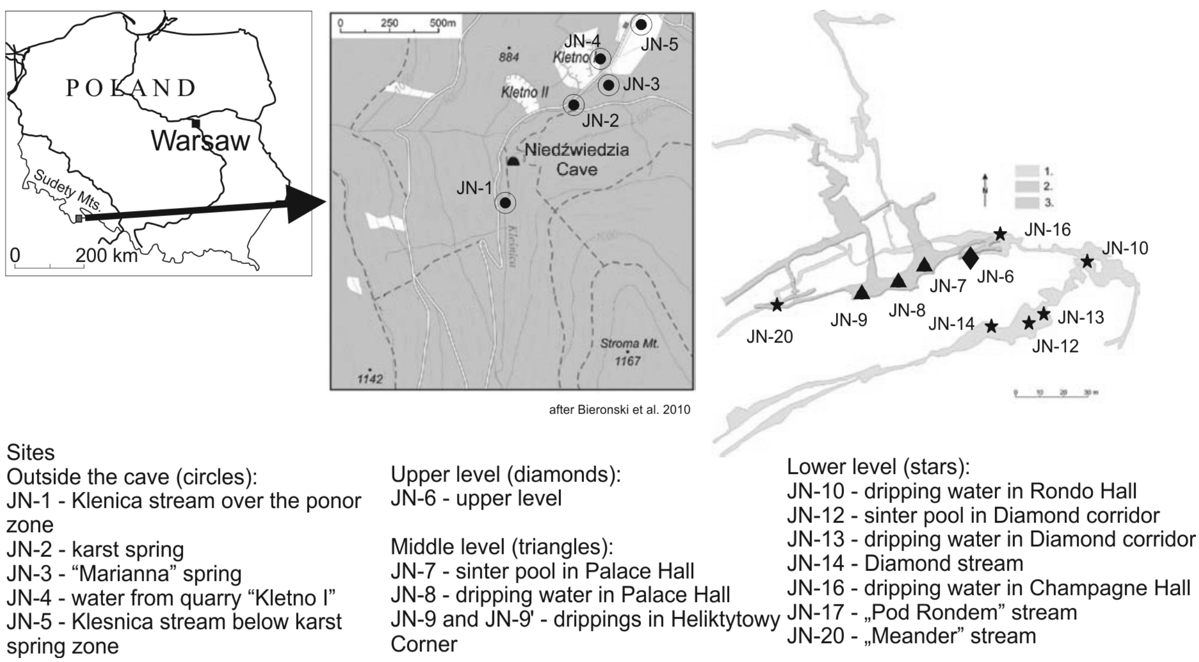

Fig. 1. *Location of study site and measurement stations in the Kleśnica valley and in the Niedźwiedzia Cave system. JN1–JN20 — localities for sample collecting and drip rate measurements.*

The water samples for this study were collected at the several sites on the surface (**Fig. 1**): precipitation in the vicinity of the cave entrance (on the roof of entrance pavilion), Kleśnica stream water in the ponor zone and water from the karst springs that drain the system. In the cave, samples of drip, pool, and stream water were collected from every level. The precipitation was recorded near the entrance to the cave. The study area is located in the mountain. If terrain morphology is complex, the amount and intensity of precipitation may significantly vary even between close located sites. So, we tried to record precipitation event as close to the cave alimentation area as possible. The drip rate was measured at 3 stations in the upper and middle levels of the cave system and at 3 stations in the lower level. The drip loggers were installed under active stalactites, which differed visually in terms of drip rate because we wished to observed the changes in drip rate among speleothems with different drip types (*i.e.*, rapid drip rates occur under larger fissures and slower rates under smaller fissures).

3. METHODS

Drip rate measurements

Drip rate was measured with acoustic loggers Stalagmate® by PiTech Research (Mattey and Collister, 2008, Mattey *et al.*, 2008). The loggers were fixed to the stalagmites growing under active stalactites located in every level of the cave system. The counts were collected in 10-minute intervals and recorded by loggers. Additionally, precipitation was measured using acoustic loggers with the same time resolution.

Tritium activity measurements

Sample preparation for tritium analyses and measurements was performed at the Institute of Geological Sciences, PAS in Warsaw. The water samples for tritium activity measurements were collected in 1.5 dm^3 polypropylene bottles. Subsamples of 0.3 dm^3 were distilled with the "Hei-VAP Precision" vacuum distillation system made by Heidolph. The distilled samples were enriched in tritium by electrolysis. We used an electrolytic procedure and equipment similar to that described by Baeza *et al.* (1999). The distilled water samples were put into electrolytic cells with an addition of 10 ml of 20% NaOH solution as an alkaline medium favourable to electric conduction. The electrolysis was conducted with a constant current of 5.5 A over 168 h at a temperature of 1–2°C. A dead water sample and standard tritium spiked water sample were prepared the same way as the natural samples to act as control samples. After electrolysis, the tritium concentrations in the samples were enriched ~15–20 times. After electrolysis, 15 ml of subsample was distilled again due to remove the sodium hydroxide and mixed in Teflon® vials with the liquid scintillator ULTIMA GOLD LLT (by Perkin Elmer) in a proportion of 8:12. The tritium activity measurements were performed with an ultralow-background spectrometer Quantuls 1220, with a total measurement time of 1275 minutes (85 cycles at 15 minutes). The dead water and spiked water samples (PerkinElmer "Tritiated Water") of the radioactivity of 44 ± 0.713 MBq kg^{-1} (on 4/19/2010) were measured with every series of environmental samples to serve as controls during the procedure. The counting efficiencies were 27.6 ± 1.2 %, with a background of 1.512 ± 0.074 cpm. The results were recalculated to Becquerel per gram (Bq g^{-1}) and to tritium units. The uncertainty in the results is reported at the 1 sigma level and was usually below the level of 0.4 TU reported in other studies (Theodorsson, 1999).

A weighted average tritium activity for precipitation ('input water' to the system) was calculated based on the activity of samples collected at 1 or 2 months intervals and the amount of precipitation in these time periods (the quantity of precipitation acted as the weighting factor for the activity). This average activity was then used for the estimation of karstic water age, assuming that the activity in an aquifer decrease only via radioactive decay (Kluge *et al.*, 2010).

4. RESULTS

Precipitation intensity

The precipitation rate was highly variable both throughout a year and between years (**Fig. 2**). The snowfall and rainfall quantities were significantly higher in 2012 than 2011. The most prominent peak in precipitation was recorded in spring (May) and summer (September) in 2011 and in summer (August–September) in 2012. A significant input of water was also noted during snow melt in March–April 2012. The rainfall events were separated by periods without precipitation (droughts) or with snowfall events. The most prominent drought events were observed during the winter seasons. However, even then, short snowmelt episodes occurred (e.g., Jan 15, 2011 and January 2012). The longest period without rainfall during the summer season, lasted 3 weeks, was observed in the first half of August 2012.

Drip rate inside the cave

The data from the drip station in the upper level of cave (site JN6, **Fig. 2**) were available only for 2011. The drip rate at the station was very low (up to 15 drips per 10 minutes) during the winter season. More rapid dripping started on 26 May, *i.e.*, 14 days after the first prominent rainfall event. Additionally, the most prominent rainfall event, on 11 September, was affected the speleothem drip rate 5 days later. The discharge from the drip point featured an even larger temporal offset following the cessation in precipitation. The main precipitation

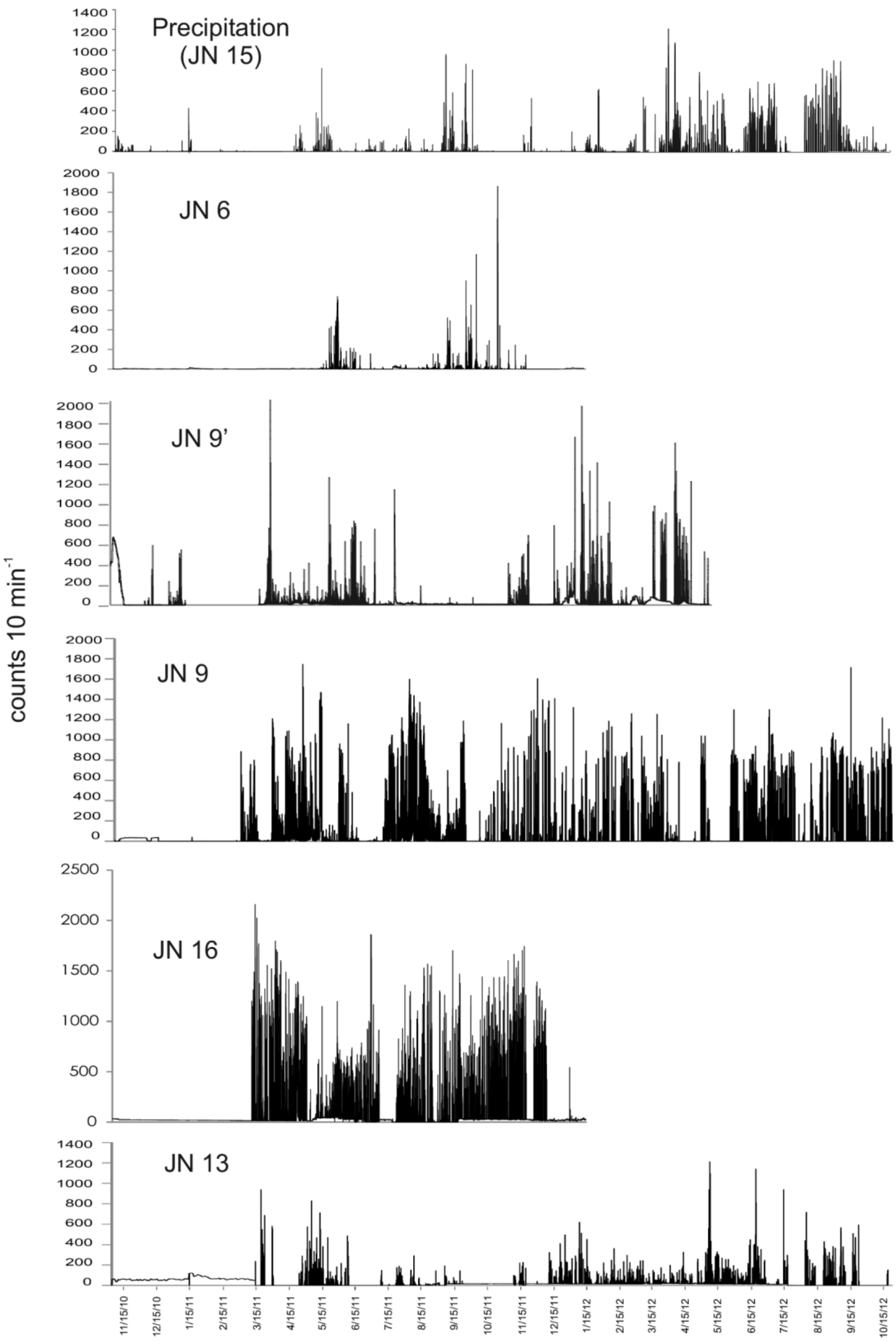

Fig. 2. *Frequency and intensity of precipitation (JN15; upper graph) and changes in discharge (counts per 10 minutes) of studied drip points inside the cave. Site codes similar to these in the Fig. 1. Horizontal scale (time) is the same for all graphs.*

period in 2011 ended on 5 October, but the peak in discharge was observed on 27 October and intense discharge ceased on 22 November, representing a 47-day offset.

Much longer offsets between precipitation and drip rate were observed in the station in the middle level of cave (site JN9', **Fig. 2**). The first increase in discharge at the middle level station that correlated with a precipitation event in 2011 was recorded on 6 November, which is relatively late (**Fig. 2**). The earlier record from this station started with a high drip rate, which did not correspond to 2011 precipitation and was probably supplied by 2010 precipitation water. This two periods of altered dripping were separated by a period (August–October 2011) with low discharge rates (11–15 drips ks^{-1}), which were likely related to the drought during the winter 2010/2011.

The second drip site in the middle level, site JN9, is located close to JN9' and represents a different discharge regime. The site featured high discharge rates throughout almost the entire measurement period, without visible correlation to precipitation intensity or periods of winter droughts. The periods of low discharge were relatively short and were not correlated with the lack of precipitation.

Similarly, the site JN16 in the Szampańska Chamber in the lower level of cave system exhibited generally high rates of discharge without clear correlation with precipitation. A short period with a low discharge rate in July 2011 might reflect winter 2010/2011.

Surprisingly, site JN13 (the drip site in the Diamond Corridor) in the lower level of the cave system much better reflected changes in precipitation intensity than site JN9 in the middle level. The record from JN13 is similar to that from site JN9' and also revealed precipitation with a greater than 6-month offset.

Tritium activity

Tritium activity varied between 3.2 ± 0.2 TU and 10.9 ± 0.4 TU (mean = 5.9 ± 1.4 TU, median = 5.7 ± 1.4 TU) (**Fig. 3**). The tritium activity of precipitation and surface water varied over the course of a year. The largest variability was observed in water from the Kletno I quarry (3.4 ± 0.2 to 10.9 ± 0.4 TU) and in precipitation samples (3.2 ± 0.2 to 9.7 ± 0.2 TU). The lowest values were observed in samples collected during the early winter season and the highest were measured in autumn samples. These differences are natural process caused by changes in solar activity (Simpson, 1960), but can be also influence by anthropogenic sources as nuclear power plants or industry (Różański *et al.*, 1991). The weighted average tritium activity of precipitation was 5.6 ± 0.2 TU, which was assumed to represent the mean activity of rainwater infiltrating into the karst system. This activity is significantly lower than 18.6 ± 4.2 TU recorded in Sudety Mountains at the end of 20^{th} century (Radwan *et al.*, 2001).

The most uniform level of activity at all stations was recorded in May 2012 (series S8, **Fig. 3A**). The Kleśnica stream water above the ponor zone (JN1, **Fig. 3B**) had a relatively high variability in activity, and the water in the karst spring zone contained low-variability activity (JN5). This pattern suggests that meteoric water mixes with karst water of more constant tritium radioactivity. The spring "Marianna" (site JN3) exhibited a relatively high diversity of tritium activity values over the course of a year. The tritium activity of water inside the cave had generally lower variability than precipitation and surface streams (**Fig. 3B**). An exception to this pattern is the sinter pools that temporary fill with water (e.g., site JN7), in which the isotopic composition is strongly modified by mixing and evaporation processes. However, permanent sinter pools (site J12) feature constant tritium activity levels during a year. The most stable activity levels were

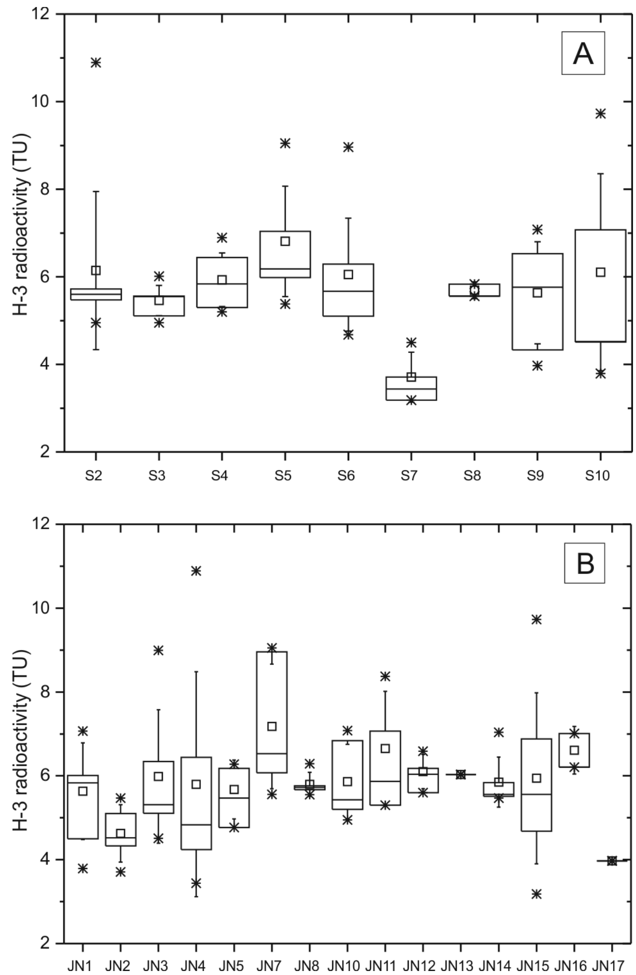

Fig. 3. *A — Tritium activity (expressed as tritium units) changes in every series of collected samples. B — Tritium activity (expressed as tritium units) changes in sample sites over entire period of study. Note that for sites JN13 and JN17 only one measurement was available. Symbol key: asterisks — minimum and maximum values; boxes range — 25, 50 and 75%; squares inside boxes — mean value; whiskers — 1 standard deviation. Series key: S2 — March 2011; S3 — May 2011; S4 — July 2011; S5 — September 2011; S6 — November 2011; S7 — January 2012; S8 — May 2012; S9 — July 2012; S10 — October 2012. Site symbols as in the Fig. 1.*

observed at the drip site in the middle level of the cave (JN8).

5. DISCUSSION

According to definitions of Smart and Friederich (1986), modified by Baker *et al.* (1997), all studied drip sites represented seasonal drips (**Fig. 4**). The maximal discharge did not exceeded 10^{-3} l s^{-1}, but the relative standard deviation of discharge was relatively high, suggesting that periods with high discharge rates were separated by periods with constant rates, low rates, or an absence of dripping. Drip sites in the cave reacted in different ways to the precipitation at every studied drip point. The best correlation between precipitation intensity and dripping rate was recorded in the upper level of the cave system. In the upper level, every major rain episode was reflected in higher drip rates. However, the reaction to the rain episode was not immediate, and delays of 5–20 days were observed. Delays were clearly visible during spring season, after the first rainfall episodes of 2011. The results suggest that the drip point JN6 in the upper level was charged from a system of cavities, which first must be filled with water infiltrating (completely or partially) before water is provided to the studied drip point. The precipitation-to-drip transition time is not directly the time of water flow from the surface to a specific drip site; more precisely, the transition time is the travel time of a wave of migrating hydraulic pressure. The response of JN6 site to precipitation is in good agreement with the karstic aquifer discharge model proposed by Fairchild *et al.* (2006). In this model, the stable low discharge rate is caused by the steady seeping of meteoric water through the soil and low-diameter fissures. During large precipitation events, water fills caverns and spills into the next cavern, connected to the drip point by larger-diameter fissures. The time of cavern filling causes offsets between precipitation and discharge at the drip site.

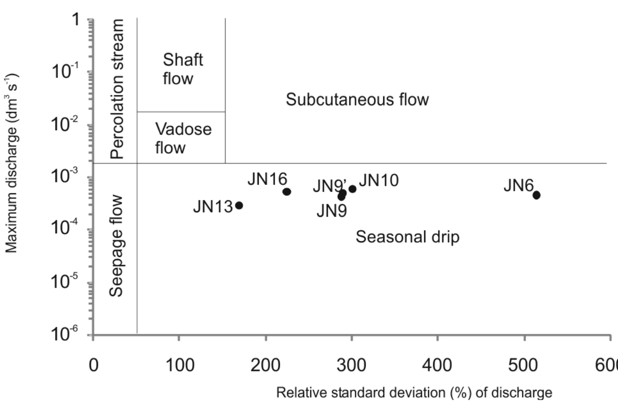

Fig. 4. *Studied drip sites position on theoretical chart of drip sites hydrological behavior by Smart and Friederich (1986). Site symbols as in the Fig. 1.*

The correlation between precipitation and discharge rate can also be observed in one of the sites in the middle level of the system (site JN9'). However, at this site, the delays between rain episodes and increases in drip rate were significantly longer and exceeded 6 months. Similar delays were not observed at the other point (JN9) in the middle level, located only 3 meters from site JN9'. The JN9 site did not respond to precipitation but did exhibit rapid changes in drip rate. These observations suggest that the JN9 site was sourced with water stored in large cavities rather than in the rock matrix. These cavities can be recharged by mixing water from different rain episodes, melting of snow cover and other cavity systems and serve to episodically supply the drip point.

A pair of drip sites that represent different modes of discharge were studied in the lower level of the cave. The discharge record of site JN13 can be correlated with precipitation. The lag between rainfall episodes and drip rate peaks is estimated to be greater than 6 months, similar to site JN9' in the middle cave level. This result is surprising because site JN13 is located 40 m lower than JN9' and suggests that JN13 is supplied by cavity recharge via hydraulically connected fissures that can originate in the middle level of the cave. In contrast, the discharge mode of site JN16 showed no correlation with precipitation and is analogous to JN9.

The estimation of transition times for drip water in the middle and lower level could be supported by tritium activity measurements. The mean value of ^{3}H activity in precipitation is higher than in other sites, excluding two sites (JN7 and JN12) inside the cave (**Fig. 3**). These sites are sinter pools, and the higher tritium activities in these pools can be caused by isotopic fractionation during the evaporation of stagnant water. Therefore, the tritium age cannot be estimated for such type of sites. Tritium activity values that were higher than in precipitation were also observed in one drip site in the lower level of the cave. For certain sites, *i.e.*, drip water, the tritium activity of cave stream and karst spring water is less variable than in precipitation, and the tritium values can indicate the mixing of "young" meteoric and "old" karst water.

We would like to stress that tritium age estimates can be made only with high uncertainty. The uncertainty is caused by high intra-annual diversity of ^{3}H activity in precipitation. More certain calculations could be performed only with longer series of tritium activity measurements and correlations between activity peaks in rain and drip water (Kluge *et al.*, 2010).

The drip water H-3 radioactivity of sites in the middle and lower levels confirmed conclusions based on discharge rate records. The activity levels of certain water samples are equal to those of precipitation, but in other cases (e.g., site JN8 in the middle level and JN10 in the lower level of the cave), the tritium activity was significantly lower. At these latter sites, the tritium age was estimated to be 0.6 ± 0.2 yr. The oldest tritium age (3.9 ± 0.6 yr) was estimated for karst spring water (site

JN2) in the winter. No other sample yielded a similar age. This result suggests that this karst spring is also sourced with "old" water, probably from deeper circulation paths. During the winter period, the input of "young" rainwater is small, and the signal from "old" water becomes significant. The age of this water is similar to the tritium age of water from the nearby "Marianna" spring, as reported by Ciężkowski *et al.* (2009). The Marianna spring is, in fact, a well that produces artesian water in the Kleśnica stream valley. However, recent samples of water from the Marianna spring have yielded tritium activity levels similar to that of precipitation. The changes in the age of water from the Marianna spring may be related to changes in water circulation patterns: water that earlier fed the Marianna spring has now been replaced with younger infiltration water, and the discharge point for the "old" karst water has become the karst spring (JN2).

6. CONCLUSIONS

Drip rate changes can be efficient tool to study the transition time of infiltrating water. Measurements of the drip rates in a series of sites help us to better understand the complexity of karst systems. In the specific case of the Niedźwiedzia Cave system, large spatial and temporal changes in discharge rates were recorded.

Longer series of tritium activity measurements in precipitation are necessary to better estimate the age of water due to the low tritium activity in the atmosphere. Fifty years after the peak of atomic testing, tritium cannot be applied as a direct temporal indicator but can be used as an isotopic tracer due to seasonal and annual changes in its activity. In the Niedźwiedzia Cave system, the minimum time series required for tritium dating of karst water is estimated to be 4 years, which is the oldest age of water observed in the karst system. Additionally, a larger initial size of water samples can help to increase the precision of tritium measurements and age calculations (Theodorsson, 1999).

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REFERENCES

Baeza A, Garcia E and Miro C, 1999. A procedure for the determination of very low activity levels of tritium in water samples. *Journal of Radioanalytical and Nuclear Chemistry* 241: 93–100, DOI 10.1007/BF02347294.

Baker A, Barnes WL and Smart PL, 1997. Stalagmite drip discharge and organic matter fluxes in Lower Cave Bristol. *Hydrological Processes* 11: 1541–1555, DOI 10.1002/(SICI)1099-1085(199709)11:11<1541::AID-HYP484>3.0.CO;2-Z.

Bieroński J, Stefaniak K, Hercman H, Socha P and Nadachowski A, 2009. Palaeogeographic and palaeoecological analysis of sediments of the Niedźwiedzia Cave in Kletno. In: Stefaniak K., Tyc A. and Socha P. (Eds), *Karst of the Częstochowa Upland and of the Eastern Sudetes*. Studies of the Faculty of Earth Sciences University of Silesia, 401–422.

Ciężkowski W, Buczyński S, Rzonca B, Marszałek H, Wąsik M and Staśko S, 2009. Groundwater of karst terrain in the Sudetes. In: Stefaniak K., Tyc A. and Socha P. (Eds), *Karst of the Częstochowa Upland and of the Eastern Sudetes*. Studies of the Faculty of Earth Sciences University of Silesia, 371–384.

Clark ID and Fritz P, 1997. *Environmental Isotopes in Hydrogeology*, Lewis Publishers, New York, 328 pp.

Craig H and Lal D, 1961. The production rate of natural Tritium. *Tellus* 13: 85–105.

Fairchild IJ, Tuckwell GW, Baker A and Tooth AF, 2006. Modelling of dripwater hydrology and hydrogeochemistry in a weakly karstified aquifer (Bath, UK): implications for climate change studies. *Journal of Hydrology* 321: 213–231, DOI 10.1016/j.jhydrol.2005.08.002.

Ford D and PD Williams, 2007. *Karst Hydrogeology and Geomorphology*. John Wiley & Sons, 576 pp.

Kluge T, Riechelmann DFC, Wieser M, Spotl C, Sultenfus J, Schroder-Ritzrau A, Niggemann S and Aeschbach-Hertig W, 2010. Dating cave drip water by tritium. *Journal of Hydrology* 394: 396–406, DOI 10.1016/j.jhydrol.2010.09.015.

Lucas LL and Unterweger MP, 2000. Comprehensive Review and Critical Evaluation of the Half-Life of Tritium. *Journal of research of the National Institute of Standards and Technology* 105: 541–549, DOI 10.6028/jres.105.043.

Mattey D and Collister C, 2008. High resolution measurement of drip discharge rates in caves using an acoustic drip counter. *Cave Radio and Electronics Journal* 70: 11–13.

Mattey D, Lowry D, Duffet J, Hodge E and Frisia S, 2008. A 56 year seasonally resolved oxygen and carbon isotope record from a modern Gibraltar speleothem: reconstructed dripwater and relationship to local precipitation. *Earth and Planetary Science Letters* 269: 80–95, DOI 10.1016/j.epsl.2008.01.051.

Ozyurt NN and Bayari CS, 2005. Steady- and unsteady-state lumped parameter modeling of tritium and chlorofluorocarbons transport: hypothetical analyses and application to an alpine karst aquifer. *Hydrological Processes* 19: 3269–3284, DOI 10.1002/hyp.5969.

Price RM, Top Z, Happell JD and Swart PK, 2003. Use of tritium and helium to define groundwater flow conditions in Everglades National Park. *Water Resources Research* 39: 1267, DOI 10.1029/2002WR001929.

Radwan I, Pietrzak-Flis Z and Wardaszko T, 2001. Tritium in surface waters, tap water and in precipitation in Poland during the 1994–1999 period. *Journal of Radioanalytical and Nuclear Chemistry* 247: 71–77, DOI 10.1023/A:1006775300812.

Różański K, Gonfiantini R and Araguas-Araguas L, 1991. Tritium in the global atmosphere: distribution patterns and recent trends. *Journal of Physics G: Nuclear and Particle Physics* 17: S523, DOI 10.1088/0954-3899/17/S/053.

Simpson JA, 1960. The production of tritons and C14 in the terrestrial atmosphere by solar protons. *Journal of Geophysical Research* 65: 1615–1616, DOI 10.1029/JZ065i005p01615.

Smart PL and Friederich H, 1986. Water movement and storage in the unsaturated zone of a maturely karstified aquifer, Mendip Hills, England. *Proceedings of the Conference on Environmental Problems in Karst Terrains and their Solutions.* National Water Wells Association, Bowling Green, Kentucky pp. 57–87.

Theodorsson P, 1999. A review of low-level tritium systems and sensitivity requirements. *Applied Radiation and Isotopes* 50: 311–316, DOI 10.1016/S0969-8043(97)10153-1.