Z. Dt. Ges. Geowiss. (J. Appl. Reg. Geol.), **172 (1)**, p. 73–82, 6 figs., 4 tables
Published online March 2021

Hydrochemical response of spring and mine waters in the Upper Harz Mountains (Germany) after dry periods and heavy rain events

Elke Bozau[1], Georg Bauer[2], Tobias Licha[3] & Sonja Lojen[4]*

Bozau, E., Bauer, G., Licha, T. & Lojen, S. (2021): Hydrochemical response of spring and mine waters in the Upper Harz Mountains (Germany) after dry periods and heavy rain events. – Z. Dt. Ges. Geowiss., 172: 73–82, Stuttgart.

Abstract: Hydrochemical observations in the Upper Harz Mountains from 2010 up to 2020 allowed for the investigation of chemical changes after extreme hydrological events. The extreme weather periods with heavy rain (e.g., July 2017) and long dryness (September 2016, May–November 2018) did not lead to formerly unobserved, unexpected changes in the hydrochemical signature of the springs and adits of the Upper Harz Mountains. After extreme weather events hydrochemical parameters are within the range of seasonal changes. The investigated water systems behave hydrochemically insensitive with respect to the parameters studied. Changes in specific electrical conductivities, major ion concentrations and $\delta^{18}O$ values of the spring and adit waters can be explained by a combination of variable rain water input and residence time in the individual catchment areas.

Kurzfassung: Langzeituntersuchungen (2010 bis 2020) der Oberharzer Quellen und Wasserlösestollen ermöglichen die Abschätzung des Einflusses von extremen Wetterereignissen auf hydrochemische Parameter. Die Extremwetterereignisse (Starkregen im Juli 2017, Trockenperioden im September 2016 sowie von Mai bis Oktober 2018) führten nicht zu wasserchemischen Extremwerten: Die gemessenen Parameter lagen in den bekannten jahreszeitlichen Schwankungsbereichen. Die ermittelten spezifischen elektrischen Leitfähigkeiten, die Konzentrationen der An- und Kationen sowie die $\delta^{18}O$-Werte der untersuchten Wässer lassen sich durch schwankende Niederschlagshöhen, verbunden mit den jeweiligen Verweilzeiten im Einzugsgebiet der Quelle oder des Stollens, erklären.

Keywords: dry periods, heavy rain events, SEC, $\delta^{18}O$, Harz Mountains

Schlüsselwörter: Trockenperioden, Starkregenereignisse, spezifische elektrische Leitfähigkeit, $\delta^{18}O$, Harz

1. Introduction

Global changes of climate and weather conditions influence the frequency of storms, rain water and flow rates in watersheds (Huntington 2006; Van Loon & Laaha 2015). Shifts in the timing of snowmelt runoff are also reported (Clow 2010). Decreasing discharge of springs and lower water tables in river catchments cause problems in freshwater and forest ecosystems, decrease agricultural yields and hinder the supply of drinking and industrial water in Germany (Steiner 2017). The impact on chemical water quality is still under investigation (e.g., Chiogna et al. 2018). Several studies show that especially anthropogenic land use and input from sewage treatment plants combined with lower flow rates degrade the quality of surface waters (e.g., Bhurthun et al. 2019; Shah et al. 2007). Manning et al. (2013) suggest that higher temperatures in combination with less dilution (lower volumes of dilute stream inflows) and accelerated weathering reaction rates will cause rising solute concentrations in mountain lakes and streams. Ground water quality is also expected to respond to changes of weather and climate conditions (Green et al. 2011). Reviewing several studies Whitehead et al. (2009) conclude that climate change will influence eutrophication and acidification processes as well as the concentrations of toxic substances in freshwater systems.

The Harz Mountains are the northernmost mountain range of Germany. There are several engineering systems for flood protection, drinking water supply and mining activities in this area. Nevertheless, anthropogenic impacts on the chemical quality of surface waters in the Upper Harz Moun-

*Addresses of the authors:
[1]Clausthal University of Technology, Department of Hydrogeology, Leibnizstr. 10, 38678 Clausthal-Zellerfeld, Germany (elke.bozau@tu-clausthal.de)
[2]Clausthal University of Technology, Institute of Electrical Information Technology, Leibnizstr. 28, 38678 Clausthal-Zellerfeld, Germany
[3]Ruhr-Universität Bochum, Hydrogeochemistry, Universitätsstr. 150, 44801 Bochum, Germany
[4]Jožef Stefan Institute, Environmental Sciences, Jamova 39, 1000 Ljubljana, Slovenia

DOI: 10.1127/zdgg/2021/0259
E. Schweizerbartsche Verlagsbuchhandlung, Stuttgart, Germany, www.schweizerbart.de

tains are almost negligible. Therefore, these waters should display the “natural” range of chemical changes in water systems according to weather and climate variations. We use long-term measurements starting in 2010 (Bozau et al. 2013) to evaluate the impact of extreme dry periods (September 2016 and May–November 2018) and heavy rain events (e.g., July 2017) on the quality of spring and mine water in the Upper Harz Mountains. As demonstrated in many hydrological studies (e.g., O’Driscoll et al. 2005; Penna et al. 2014), specific electrical conductivity (SEC) and stable isotopes of water are useful parameters to characterise the recharge rate, residence time distribution and catchment size of springs and aquifers. The validity of SEC as a proxy for the content of total dissolved ions in water samples (e.g., McNeil & Cox 2000) is also supported by the investigation of seasonal chemical variations of the water composition in the Harz Mountains discussed in Bozau et al. (2013, 2017). Therefore, our study concentrates on SEC and $\delta^{18}O$ values to allow a fast and easy evaluation of the water dynamics in the study area after extreme weather periods.

2. Study area

The Harz Mountains (Fig. 1), known for ancient silver and base metal mining, are an important drinking water supply region for Northern Germany today. Geologically the mountain range belongs to the Rhenohercynian Zone of the Variscan orogenic belt. Former mining activities have caused local contaminations of surface waters as well as recharge areas. But the majority of waters is not chemically affected by mining. There are two main systems of water management in the Western Harz Mountains. A lot of springs and creeks are involved in the management system “Oberharzer Wasserregal”, which is an old engineering system of dams, adits, reservoirs and ditches. It was constructed mainly from the 16th to 19th centuries to deliver water to the water wheels of the mines. Reservoirs for flood protection, hydroenergy production and drinking water supply were built in the 20th century. The six big reservoirs of the western Harz Mountains (Ecker-, Innerste-, Grane-, Oder-, Oker- and Söse-Stausee) have a water storage capacity of about 185,000,000 m^3 (HWW 2021).

The water quality of the Harz Mountains is mainly influenced by atmospheric deposition, water rock interactions and biological activity. Current anthropogenic influences are minor. Even elevated dissolved metal concentrations in surface water from past mining sites are rarely found (Bozau et al. 2013 and 2017).

As already known from hydrological observations (Lange 2012) climate change will lead to larger seasonal variations of the runoff in the Harz Mountains. Summertime is getting drier, resulting in lower runoff, whereas runoff volumes are rising in winter. The 2018 European drought with low precipitation from April until October significantly affected the runoff from the Harz Mountains. The water table of the dam reservoirs decreased to alarming levels.

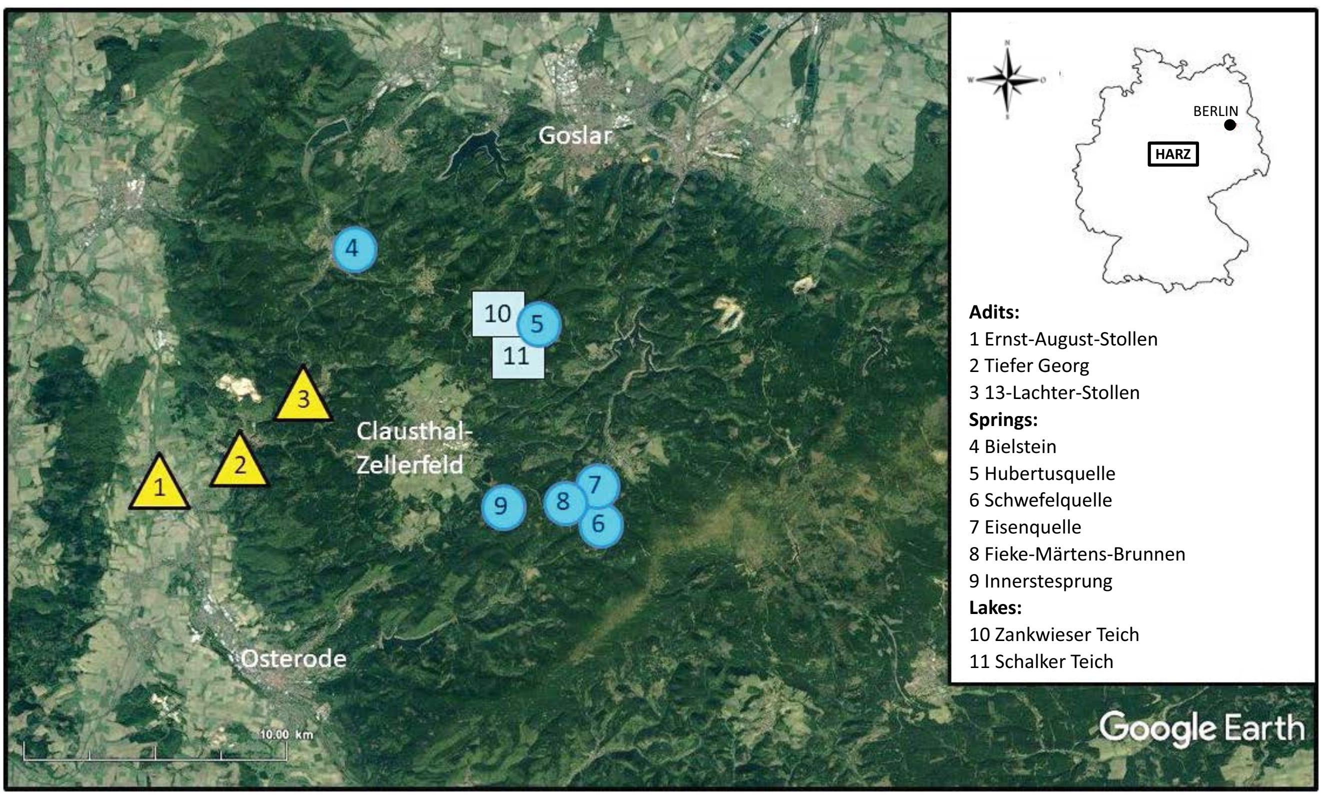

Fig. 1: Study area with sampling points for spring, lake and adit water.

3. Sampling points and methods

Based on continuous investigations of surface waters in the Upper Harz Mountains distinct sampling locations were chosen to evaluate the effect of the long dry period in 2018. Water of six springs (Bielstein, Hubertusquelle, Innerstesprung, Eisenquelle, Schwefelquelle and Fieke-Märtens-Brunnen), located in the geological unit "Clausthaler Kulmzone" mainly consisting of shales and greywackes at elevations up to 700 m a.s.l., were sampled (Fig. 1). Furthermore, the three main drainage adits of the mine area around Clausthal-Zellerfeld (Ernst-August-Stollen at Gittelde/189 m a.s.l., Tiefer Georg at Bad Grund/286 m a.s.l. and 13-Lachter-Stollen at Wildemann/383 m a.s.l.) and two mine lakes near Clausthal-Zellerfeld were involved in the study. The surrounding rocks of all sampling points are shales and greywackes. The adit water is additionally in contact with the remaining ores of the old mines. The deeper adits (Ernst-August-Stollen, Tiefer Georg) at the edge of the mountain range also drain Permian rocks (mainly limestone).

The water of all locations was directly sampled after the first rain event in October 2018. In November 2018, the springs "Innerstesprung" and "Hubertusquelle" dried out again. A second water sampling campaign took place in December 2018. The sampling points are known from older studies and are described in Hinze (1971) and Bozau et al. (2013 and 2017). Temperature, pH value, specific electrical conductivity (SEC) were measured in the field. Major ions and isotope data ($\delta^{18}O$ and $\delta^{2}H$) were analysed according to the methods given in Bozau et al. (2013) and compared with older data. The stable isotopic composition of water was determined by the H_2O-H_2 equilibration method (^2H) with an analytical expression of ±0.8 ‰ and the H_2O-CO_2 equilibration method (^{18}O) with an analytical precision of ±0.1 ‰. The measured isotope ratios are expressed as delta notations relative to the Vienna Standard Mean Ocean Water (VSMOW). The SEC values are corrected for temperature. The analytical error of the SEC measurements is about 1 µS/cm.

4. Results and discussion

4.1 Hydrological observations

The average temperatures and precipitation rates per month measured at the TU Clausthal (IEI) for 2016–2018 are given in Fig. 2 and are compared to the data measured for the period from 1961–1990 which are delivered by the German

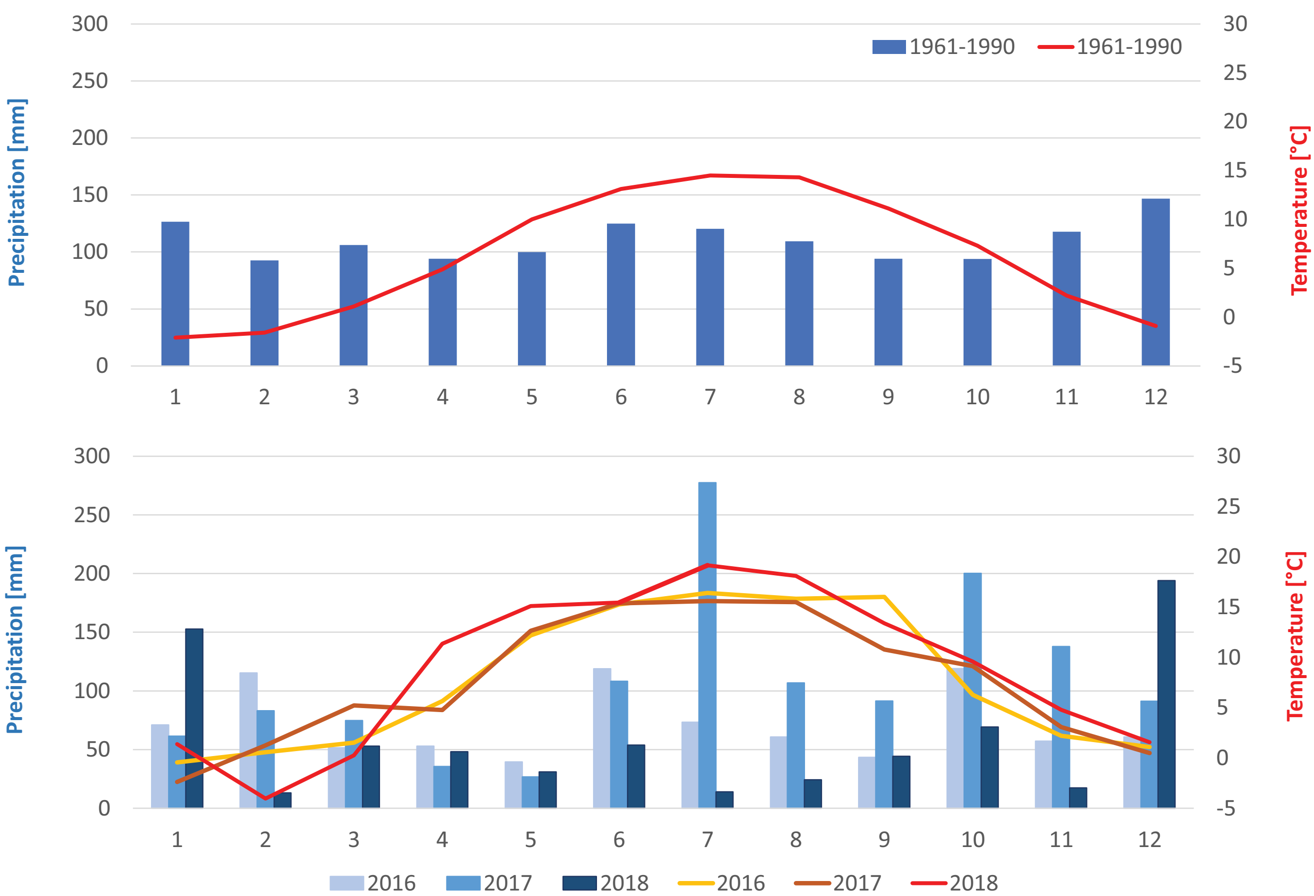

Fig. 2: Average monthly temperature and precipitation data for Clausthal-Zellerfeld in 2016, 2017 and 2018 measured at the TU Clausthal (IEI) compared to data for 1961–1990 (DWD).

Weather Service (DWD). The annual precipitation rate is 864 mm for 2016, 1295 mm for 2017 and 715 mm for 2018. Distinct seasonal differences in the monthly rates are found: 278 mm rain was falling in July 2017 whereas one year later in July 2018 almost no real rain event took place. A precipitation rate of only 14 mm was measured. The average value for July from 1961–1990 is 120 mm.

During the hydrochemical observations starting in 2010, only the adit “13-Lachter-Stollen”, the springs “Innerstesprung” and “Hubertusquelle” dried out. Other springs (e.g., spring “Bielstein”) and mine adits (e.g., adit “Ernst-August-Stollen”) with large catchment areas slowly reacted to weather events, whereas springs and adits with small catchment sizes and mainly connections to surface runoffs showed broader variations of the discharge rates. In 2018, only two of the investigated springs (Innerstesprung, Hubertusquelle) dried out. After the long dry period from May to the end of October, these springs were filled by precipitation, but dried out again in November 2018. First, the precipitation amounts in December led to a continuous discharge of these springs.

Normally, the spring “Innerstesprung” is earlier dry and reacts faster after rain events than the spring “Hubertusquelle”. This different behaviour after dry periods can be explained by the catchment size of the two springs. The larger catchment size of the spring “Hubertusquelle” delays the reaction caused by changing precipitation rates whereas the water flow of the spring “Innerstesprung” directly reacts after extreme dry periods and the first rain events after dryness.

The water table of mine lakes obviously dropped during the dry period in 2018. According to our knowledge, a drying out of the lakes has not been observed for more than 100 years. However, there are historical documents (Schmidt 2007) stating that the lake “Hirschler Teich” fell dry during the drought in 1766/67 leading to severe problems in the mines.

4.2 Hydrochemical characteristics of spring, adit and lake water

Extreme hydrological situations lead to chemical changes of spring and adit waters. High specific electrical conductivities (SEC) and ion concentrations are observed after dry periods. Heavy rain events lead to a dilution of the water as seen in lower ion concentrations. But the chemical changes after the recent extreme hydrological periods do not exceed the observed long-term variations of the water composition studied in the Upper Harz Mountains. Concerning extreme dry periods the chemical state of spring and adit water seems to be insensitive. The water composition after the heavy rain event in 2017 is comparable to values measured after, for instance, the snow melt in March 2012 (Bozau et al. 2013). The first discharge after dry periods (so called “first flush” events) does not lead to unexpectedly high concentrations in the investigated spring water of the Upper Harz Mountains. This may be different in other areas; Nordstrom (2009) predicts higher average concentrations at mine sites in the USA.

Specific electrical conductivity (SEC), constituting an integrated signal of major cations and anions, was used as the main parameter to characterise changes of spring, lake and adit water composition and quality caused by dry periods as well as heavy rain events (Table 1, Figs. 3a, b).

High values of SEC were found after dry periods whereas rain events and snow melt dilute the spring water leading to lower SEC values. These seasonally changing SEC values are more significant in the springs with smaller catchment areas and shorter residence time of the water, such as at spring “Innerstesprung”. In addition to the data given in Table 1, all measurements of pH values and SEC data taken from 2010 to 2020 for this spring are shown in Fig. 3a.

Isotope data ($\delta^{18}O$ and $\delta^{2}H$) do not always correlate with SEC (Figs. 3d, 5), but can be used for the estimation of the extent of the catchment area of springs and adits.

Average monthly $\delta^{18}O$ values in precipitation from the Global Network of Isotopes in Precipitation (GNIP) are shown for two stations near the Harz Mountains (Fig. 4). Braunschweig is situated about 60 km north of the study area at 75 m a.s.l. and the isotope ratios display higher values than in the study area. The topographic effect of the mount “Wasserkuppe” (about 200 km south of the study area and 950 m a.s.l.) is seen in lower isotope ratios and should be comparable for the sampling sites in the study area with maximum altitudes of about 750 m a.s.l. The monthly variation of isotope ratios in precipitation and their average values are pre-

Table 1: Water composition variations of the springs during the period of 2010–2018 (measured by SEC). The specific values measured in October 2018 after the dry period are shown; these values display the maximum values measured in two springs (Hubertusquelle, Eisenquelle). *Data from Alicke (1974) added. **Value measured after the flood in 2017.

	Innerstesprung	**Hubertusquelle**	**Bielstein**	**Eisenquelle***	**Schwefelquelle**	**Fieke-Märtens-Brunnen**
Number of samples	29	6	8	16	9	7
SEC [µS/cm]						
Min	57**	185	234	61	228	153
Max	98	340	307	171	631	262
Mean	78	252	271	99	366	182
October 2018	97	340	290	171	344	160
Dried out in	2016, 2018	2016, 2018	Not observed	Not observed	Not observed	Not observed

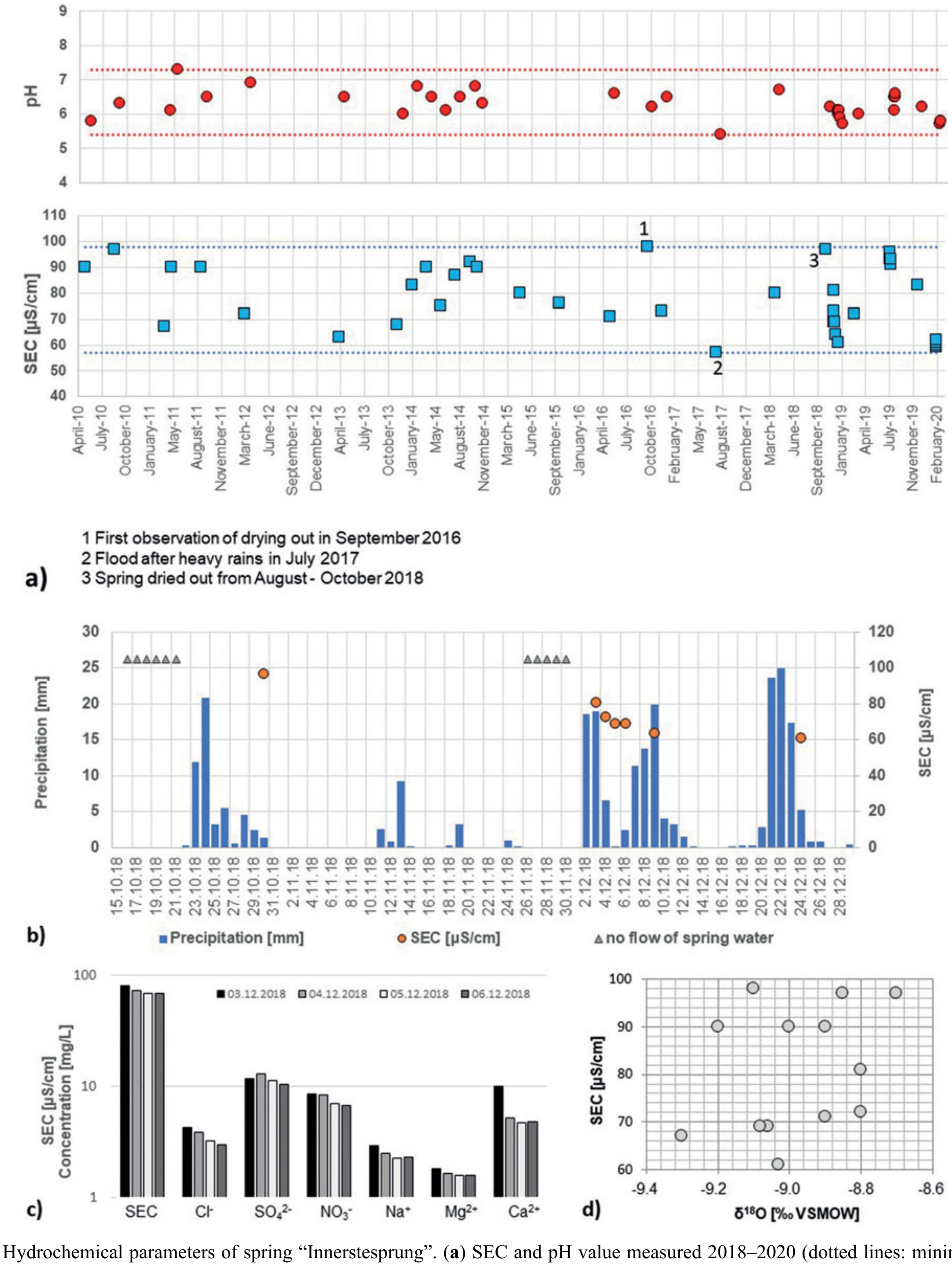

Fig. 3: Hydrochemical parameters of spring "Innerstesprung". (**a**) SEC and pH value measured 2018–2020 (dotted lines: minimum and maximum values). (**b**) Precipitation rates and SEC of spring "Innerstesprung" measured in 2018. Days when the spring was dried out are indicated by grey triangles. (**c**) Major ions and SEC measured in December 2018; the concentrations are decreasing after the dry period with increasing rain amounts. (**d**) SEC vs. $\delta^{18}O$ measured 2010–2018.

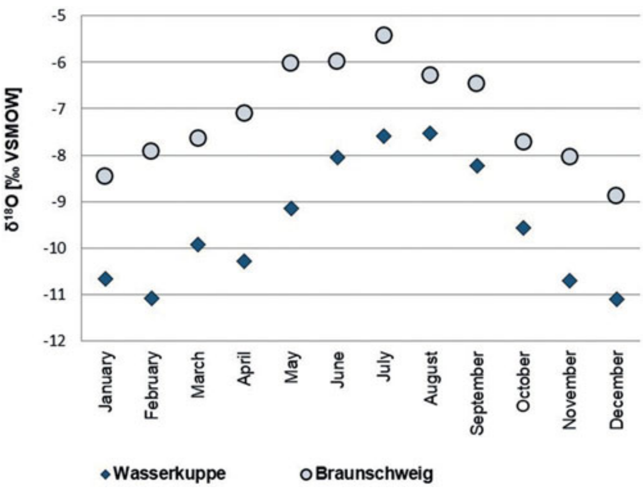

Fig. 4: Average $\delta^{18}O$ values of monthly precipitation at the German GNIP stations "Braunschweig" (1978–2016) and "Wasserkuppe" (1978–2013).

served during the soil passage and can be found in surface and upper ground waters (Richter 1987).

Constant isotope ratios displaying average rain water concentrations are typical for springs and adits with large catchment areas (Schwarz et al. 2009; Bozau et al. 2013). One spring (Bielstein) with a relatively large and homogeneous catchment area has nearly constant $\delta^{18}O$ and $\delta^{2}H$ values (comparable to average precipitation values) measured in different seasons and after extreme weather conditions, whereas most of the springs show seasonal variations of these values. In general, the $\delta^{18}O$ values measured in the springs are lower than the average value found in precipitation of the Harz Mountain. This observation can be explained by the main recharge time: higher precipitation amounts combined with lighter $\delta^{18}O$ values are observed in winter. Only the spring "Eisenquelle" has higher $\delta^{18}O$ values than average rain water at two sampling dates (September 2011 and October 2018). Compared to the other springs the spring "Eisenquelle" is located at the highest elevation and gets the highest precipitation input. The isotopic composition of summer rain seems to be preserved in the spring water at these sampling dates. The deepest drainage adit (Ernst-August-Stollen), collecting the water of several former mines, also displays relatively constant isotope values. There is no plausible explanation for the range of $\delta^{18}O$ values in the water of the adit "Tiefer Georg". The highest $\delta^{18}O$ value of this adit was measured directly after the drought period in 2018 (Table 2). Compared to spring waters the SEC of all investigated adits is elevated due to enhanced water-rock interaction including residual ore material (Fig. 5).

Isotope ratios characterise the evaporation state of mine lakes (Table 3 and Fig. 6; Bozau & Lojen 2017). The lakes of the Upper Harz Mountains mostly display the $\delta^{18}O$ and $\delta^{2}H$ values of precipitation and surface runoff. They are sometimes characterised by slightly heavier isotopic values due to minor evaporation effects in the Upper Harz Mountains. Only during very dry seasons (e.g., September 2016 and November 2018), evaporation effects are clearly seen in the isotope ratios. Comparing the isotope ratios of the surface water in selected mine lakes it is apparent that the highest values of $\delta^{18}O$ and $\delta^{2}H$ were not measured after the dry period in autumn 2018, as would be expected from evaporation effects. There are likely water mixing processes involved which will lead to different values in the lake profile. Distinct changes in major ions and their ratios were not found in lake waters. The SEC of 46 µS/cm measured in lake "Zankwieser Teich" in November 2018 is the maximum value during the observations of this lake. Normally, the lake water has a SEC of about 30 µS/cm and relatively constant ion concentrations and ratios during all seasons (Bozau et al. 2015b).

4.3 Conceptual model of spring water evolution

The investigated ion concentrations from the spring "Innerstesprung" allowed for distinguishing the behaviour of the major ions after a dry period in December 2018. Average rain water concentrations (measured near the spring by Bozau et al. 2015a) are much lower than the concentrations measured in the spring, as expected. Depending on the precipitation rate and atmospheric wash-out effects, the SEC of open-field precipitation ranges from 5 up to 43 µS/cm with a mean value of about 20 µS/cm. Rain water concentrations are enriched due to the interaction with vegetation (canopy throughfall). As shown in other studies (Andreae 1993) can-

Table 2: SEC and $\delta^{18}O$ of adits measured at the adit portal.

SEC [µS/cm]	January 16	May 17	October 18	December 18	March 19
Ernst-August-Stollen	1173	1131	1037	991	1060
Tiefer Georg	448	550	571	576	509
13-Lachter-Stollen	345	dry	dry	414	409
$\delta^{18}O$ [‰ VSMOW]	**May 17**	**October 18**	**December 18**	**March 19**	
Ernst-August-Stollen	-8.80	-8.88	-8.97	-8.96	
Tiefer Georg	-8.64	-8.19	-8.51	-8.79	
13-Lachter-Stollen	–	–	-8.63	-8.86	

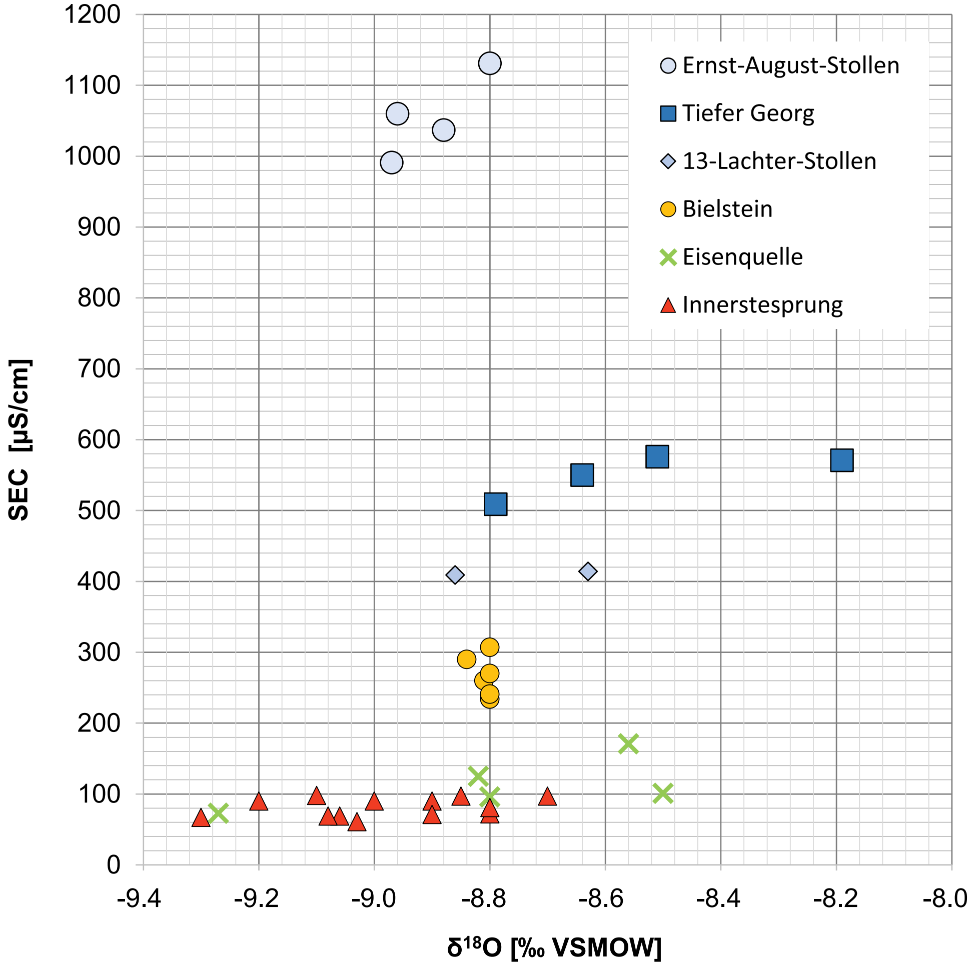

Fig. 5: SEC vs. $\delta^{18}O$ values of the springs "Bielstein", "Innerstesprung", "Eisenquelle" and the adits "Ernst-August-Stollen", "Tiefer Georg" and "13-Lachter-Stollen", measured in 2010–2019.

opy throughfall can lead to up to threefold higher SEC values than open-field precipitation due to evapotranspiration and filter effects of the forest. Furthermore, the infiltrating rain water is chemically changed in the soil and upper aquifer zones by microbiological and weathering processes (e.g., dissolution of silicate minerals). The major ions of spring water after a dry period show different trends. Chloride concentrations in the spring water continuously decrease parallel to the wash-out effect of precipitation, whereas calcium and sodium reach stable concentrations possibly due to equilibrium reactions during silicate weathering (Fig. 3c). Potassium concentrations are nearly constant at <1 mg/L and the wash out effect is not seen. Sulphate concentrations vary without trend. However, the observed data do not allow for a distinct interpretation of the geochemical processes. Only a simplified calculation of SEC values according to weather conditions and geochemical processes (combining canopy throughfall and soil weathering) can be provided (Table 4). The resulting SEC values due to wash-out effects, weathering and other exchange reactions are estimated and compared to measured minimum and maximum values which are representing the different hydrological events.

Further data of the infiltrating water in the different soil zones and direct analysis of the rain water including canopy throughfall in the catchment area, which should be measured at least daily, are necessary to understand the chemical evo-

Table 3: SEC and $\delta^{18}O$ values of mine lakes.

	May 2016		September 2016		November 2018	
Mine lake	SEC [µS/cm]	$\delta^{18}O$ [‰]	SEC [µS/cm]	$\delta^{18}O$ [‰]	SEC [µS/cm]	$\delta^{18}O$ [‰]
Zankwieser Teich	29	-6.84	32	-3.93	46	-4.50
Schalker Teich	157	-8.51	167	-7.67	167	-7.79

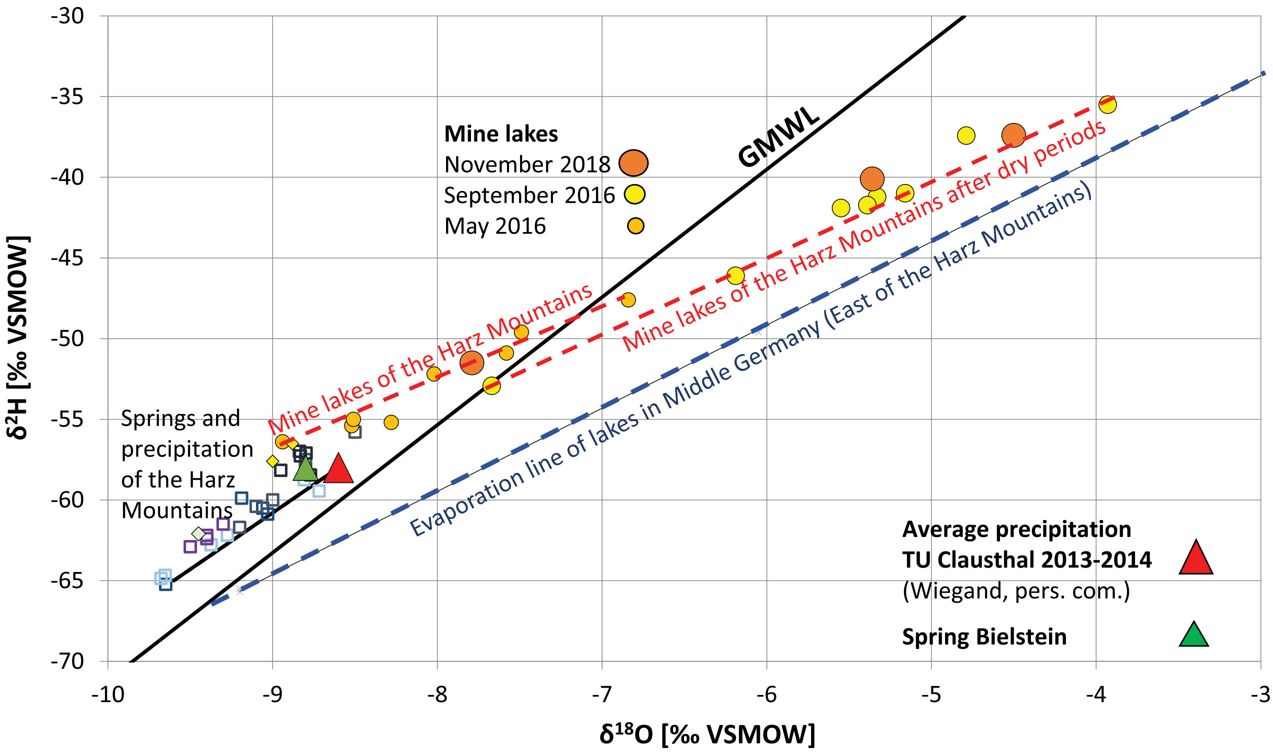

Fig. 6: Isotopic composition ($\delta^{18}O$ and δ^2H) of precipitation; springs and mine lakes from the Upper Harz Mountains compared to the Global Meteoric Water Line (GMWL) and evaporation effects measured in lakes of Middle Germany (Bozau & Lojen 2017).

Table 4: Processes changing chemical water composition from rain to spring water. Considering the measured SEC and the main known processes influencing the water composition of the spring "Innerstesprung" the following simplified calculation allows for the estimation of SEC values in the spring water after dry periods and heavy rain events (weak influence +, average/moderate influence ++, strong influence +++).

Precipitation (Open field)		**Wash-out effect**	**Evapo-transpiration**	**Soil zone and upper rock layers** Microbiological processes (e.g., nitrification) Water rock interaction (e.g., silicate weathering)	**Estimated SEC of spring water after leaving the subsurface catchment area** (compared to measured SEC)
Heavy rain event	<20 µS/cm	+	+	Short residence time: +	60 µS/cm (July 2017: 57 µS/cm)
First rain after dry period	>20 µS/cm	+++	++ (+++ Summer)	Long residence time: +++	95 µS/m (October 2018: 98 µS/cm)
Ø Precipitation	20 µS/cm	++	+	Ø Residence time: ++	80 µS/cm

lution of the spring water in more detail. These chemical investigations should be combined with flow rate measurements and the calculation of elemental loads.

5. Summary

The investigated data series show that extreme weather conditions with heavy rain events and long dry periods have not led to extreme, unpredictable changes in the chemical water composition of the springs, lakes and adits in the Upper Harz Mountains. Compared to other study areas where e.g., anthropogenic water inputs from industry and sewage treatment plant can decrease the water quality, the surface waters of the Harz Mountains do not display unexpected changes of the ion concentrations. The measured concentrations after extreme weather periods are within the known annual range with minimum values in late winter and spring after snow melt and maximum values in autumn. Following well-established techniques we have used specific electrical conductivity (SEC) measurements, representing the major ion concentrations, and $\delta^{18}O$ values as diagnostic parameters to characterise the investigated hydrochemical systems.

Water management in the study area must be preferentially focused on the runoff, water volume and storage in order to provide a continuous drinking water supply. Furthermore, continuous water release to the creeks and rivers of the foreland of the Harz Mountains must be ensured during dry periods. As seen after the heavy rain event in July 2017, local measures for flood prevention are also necessary. An impact of additional long-term climate-change effects on water quality (e.g., changes of forest vegetation and subsurface biogeochemical reactions) are possible and should be investigated in interdisciplinary studies.

6. Acknowledgements

We thank M. Rittmeier (University of Göttingen) for analysing the major ions by IC, M. Josuweit and J. Metzner (TU Clausthal) for sampling spring and adit water in 2018, B. Wiegand (University of Göttingen) for providing the average isotope data for rain water sampled in Clausthal in 2014. We also thank the two anonymous reviewers and Jonas Kley for the careful reading of our manuscript and the valuable comments.

7. References

Alicke, R. (1974): Die hydrochemischen Verhältnisse im Westharz in ihrer Beziehung zu Geologie und Petrographie. – Clausthaler Geol. Abh., 20: 1–223.

Andreae, H. (1993): Verteilung von Schwermetallen in einem forstlich genutzten Wassereinzugsgebiet unter dem Einfluß der atmosphärischen Deposition am Beispiel der Sösemulde (Westharz). – Ber. Forschungszentr. Waldökosyst., A 99: 1–161.

Bhurthun, P., Lesven, L., Ruckebusch, C., Halkett, C., Cornard, J.-P. & Billon, G. (2019): Understanding the impact of the changes in weather conditions on surface water quality. – Sci. Total Environ., 652: 289–299.

Bozau, E. & Lojen, S. (2017): Interaction between spring waters and mining lakes in the Upper Harz Mountains (Germany) – An isotope-hydrochemical approach. – Book of abstracts, 14th Workshop European Society for Isotope Research, 25–29 June 2017, Băile Govora, Romania.

Bozau, E., Stärk, H.-J. & Strauch, G. (2013): Hydrogeochemical characteristics of spring water in the Harz Mountains, Germany. – Geochemistry, 73: 283–292.

Bozau, E., Azoños Figueroa, A., Licha, T. & Wiegand, B. (2015a): Chemische Zusammensetzung des atmosphärischen Eintrags, Messstation Clausthal-Zellerfeld (Harz), Oktober 2013 – November 2014. – Grundwasser, 20: 163–168.

Bozau, E., Licha, T., Stärk, H.-J., Strauch, G., Voss, I. & Wiegand, B. (2015b): Hydrogeochemische Studien im Harzer Einzugsgebiet der Innerste. – Clausthaler Geowiss., 10: 35–46.

Bozau, E., Licha, T. & Ließmann, W. (2017): Hydrogeochemical characteristics of mine water in the Harz Mountains, Germany. – Geochemistry, 77: 614–624.

Chiogna, G., Skrobanek, P., Narany, T.S., Ludwig, R. & Stumpp, C. (2018): Effects of the 2017 drought on isotopic and geochemical gradients in the Adige catchment, Italy. – Sci. Total Environ., 645: 924–936.

Clow, D.W. (2010): Changes in the timing of snowmelt and streamflow in Colorado: A response to recent warming. – J. Climate, 23: 2293–2306.

DWD – German Weather Service, Climate data center; https://cdc.dwd.de/portal/.

GNIP – Global Network of Isotopes in Precipitation; https://nucleus.iaea.org/wiser/index.aspx.

Green, T.R., Taniguchi, M., Kooi, H., Gurdak, J.J., Allen, D.M., Hiscock, K.M., Treidel, H. & Aureli, A. (2011): Beneath the surface of global change: Impacts of climate change on groundwater. – J. Hydrol., 405: 532–560.

Hinze, C. (1971): Geologische Karte von Niedersachsen 1: 25.000, Erläuterungen zu Blatt Clausthal-Zellerfeld Nr. 4128: 166 p.; Hannover (Niedersächs. Landesamt Bodenforsch.).

Huntington, T.G. (2006): Evidence for intensification of the global water cycle: Review and synthesis. – J. Hydrol., 319: 83–95.

HWW – Harzwasserwerke (2021): https://www.harzwasserwerke.de/infoservice/aktuelle-talsperrendaten/?zeit=heute.

IEI – Institute of Electrical Information Technology, TU Clausthal; https://www.iei.tu-clausthal.de/wetter/.

Lange, A. (2012): Hydrologische Untersuchungen im Westharz mit Blick auf ein sich änderndes Klima. – Schriftenr. a. d. Nationalpark Harz, 10: 5–9.

Manning, A.H., Verplanck, P.L., Caine, J.S. & Todd, A.S. (2013): Links between climate change, water-table depth, and water chemistry in a mineralized watershed. – Appl. Geochem., 37: 64–78.

McNeil, V.H. & Cox, M.E. (2000): Relationship between conductivity and analysed composition in a large set of natural surface-water samples, Queensland, Australia. – Environ. Geol., 39: 1325–1333.

Nordstrom, D.K. (2009): Acid rock drainage and climate change. – J. Geochem. Explor., 100: 97–104.

O'Driscoll, M.A., DeWalle, D.R., McGuire, K.J. & Gburek, W.J. (2005): Seasonal ^{18}O variations and groundwater recharge for three landscape types in central Pennsylvania, USA. – J. Hydrol., 303: 108–124.

Penna, D., Engel, M., Mao, L., Dell'Agnese, A., Bertoldi, G. & Comiti, F. (2014): Tracer-based analysis of spatial and temporal variations of water sources in a glacierized catchment. – Hydrol. Earth Syst. Sci., 18: 5217–5288.

Richter, W. (1987): Deuterium and oxygen-18 in Central European groundwaters. – Isotopes Environ. Health Stud., 23 (11): 385–390.

Schmidt, M. (2007): WasserWanderWege. Ein Führer durch das Freilichtmuseum, Kulturdenkmal Oberharzer Wasserregal: 230 p.; Clausthal-Zellerfeld (Pieper).

Schwarz, K., Barth, J.A.C., Postigo-Rebollo, C. & Grathwohl, P. (2009): Mixing and transport of water in a karst catchment: A case study from precipitation via seepage to the spring. – Hydrol. Earth Syst. Sci., 13: 285–292.

Shah, V.G., Dunstan, R.H., Geary, P.M., Coombes, P., Roberts, T.K. & Rothkirch, T. (2007): Comparison of water quality parameters from diverse catchments during dry periods and following rain events. – Water Res., 41: 3655–3666.

Steiner, A. (2017): Niedrigwasser und Trockenheit: Auswirkungen und Maßnahmen der Wasserwirtschaft in Bayern. – Tagungsband 8. Agrarwiss. Symp. „Herausforderung Klimawandel", 21.09.2017, Freising-Weihenstephan, Hans-Eisenmann-Zentrum; http://www.hez.wzw.tum.de/fileadmin/Agrarwissenschaftliches_Symposium/AgrarSymp_2017/2017_Tagungsband_final.pdf.

Van Loon, A.F. & Laaha, G. (2015): Hydrological drought severity explained by climate and catchment characteristics. – J. Hydrol., 526: 3–14.

Whitehead, P.G., Wilby, R.L., Battarbee, R.W., Kernan, M. & Wade, A.J. (2009): A review of the potential impacts of climate change on surface water quality. – Hydrol. Sci. J., 54: 101–123.

Manuscript received: 07.10.2020
Revisions required: 31.12.2020
Revised version received: 28.01.2021
Accepted for publication: 03.02.2021