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Short Communication

Spring water monitoring in the Upper Harz Mountains: Precipitation, runoff and specific electrical conductivity

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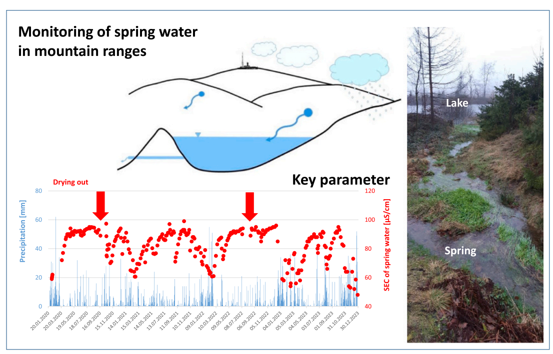
HIGHLIGHTS

- Spring water has been monitored for 4 years including 2 drying out events.
- A specific relation of precipitation, runoff and SEC is found at the spring.
- Extreme weather events and deforestation did not change the runoff-SEC ratio.
- Precipitation amounts for the first flush event were quantified.
- Major ions compared to SEC indicate different sources for the water composition.

GRAPHICAL ABSTRACT



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ABSTRACT

Due to extreme weather events and deforestation the physical and chemical characteristics of watersheds in mountain areas could exceed the known variations. Therefore, the spring water of the Innerste river in the Western Harz Mountains (Germany) was monitored from 2020 to 2023. The monitoring approach is simple and can be directly transferred to other watersheds of springs which are connected to the meteoric water cycle.

The specific electrical conductivity (SEC) of the water is compared to daily precipitation data. The SEC values range between 50 and 100 μS/cm. In September 2020 and July 2022 the spring dried out. A hysteretic relationship between spring runoff and spring water mineralisation was found. The SEC values of the spring water are rising during dry periods or in winter seasons with a long ice cover in the catchment area. The highest SEC values are typical for long dry periods and flush events after the drying out of the spring. The relationship of SEC and major ions of the spring water (especially bicarbonate) indicates that biogeochemical processes within the soil zone and water-rock interactions in fractured shales and greywackes of the catchment area control the chemical composition of the spring water. Comparing the obtained results with data measured before the first observed drying out of the spring, no unexpected new values and correlations of runoff, SEC values and ion concentrations were found.

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1. Introduction

Climate change and the increased frequency of extreme weather events influence the runoff behaviour and the chemical characteristics of aquifers, surface and spring water (e.g., Manning et al., 2013; Van Loon and Laaha, 2015). For a better understanding of future developments spring water monitoring should be intensified (Tetzlaff et al., 2017). The specific electrical conductivity (SEC) of natural water can be easily measured in the field or may even provide real time data at low costs and has been applied as a key parameter in the study of hydrological catchment areas. The potential of SEC data for the understanding of hydrological systems is often not sufficiently appreciated. Catchment specific conversion factors for SEC values can be used to estimate the load of total dissolved solids or the concentration of single ions (e.g., Hubert and Wolkersdorfer, 2015; Zinabu et al., 2002). As shown in older studies (Alicke, 1974; Birke et al., 1995; Roostai, 1997) there is a good correlation between precipitation/runoff and SEC of the spring water in the Upper Harz Mountains (Germany). The hydrochemical response of spring and mine water in the Harz Mountains after extreme weather periods was evaluated by Bozau et al. (2021). Three mine adits and six springs of the Western Harz Mountains were investigated. It was shown that periods with heavy rain and long dryness did not lead to formerly unobserved, unexpected changes in the hydrochemical signature of the spring and adit water. After extreme weather events hydrochemical parameters (e.g., pH, SEC, main ions) are within the range of seasonal changes. During this study SEC also proved as an excellent proxy to evaluate the dynamic hydrochemical responses of spring systems to seasonal variations, extreme weather periods and climate changes. For a better evaluation of drying out and first flush events the measurements of SEC and pH were intensified at one well-known spring. The detailed observations are discussed in this study.

2. Study site and methods

The spring of the Innerste river (called "Innerstesprung") is situated near the town of Clausthal in the Upper Harz Mountains (Fig. 1). It is connected to an artificial system of creeks, lakes and adits, which was built from the 16th to 19th century for the water supply of the former mining district and is called "Oberharzer Wasserregal" (Schmidt, 1997). The catchment area consists of fractured Paleozoic shales and greywackes. The catchment of the spring was dominated by spruce forest. The trees were damaged by acid rain in the last century, the dry periods starting in 2016, and bark beetle attacks. Most of the trees were cut down in autumn and winter 2020. A new tree assemblage (e.g., mountain ash, beech) is developing. Our first water samples of the spring were taken in 2010. Major ions and trace elements including REE were analysed (Bozau et al., 2013). Later the spring was irregularly observed concentrating on pH and SEC measurements in the field. Occasionally, stable isotopes were measured by the commercial laboratory Hydroisotop GmbH, Schweitenkirchen. The DIC-13C data were analysed by isotope ratio mass spectrometry (accreditation certificate D-PL-17315-01-00) with an analytical precision of ±0.3 ‰. The measured carbon isotope ratios of the samples are expressed in delta notations ($\delta^{13}C$) as parts per thousand (‰) deviations relative to the VPDB standard.

The first drying out of the spring was recognised in September 2016. After the long dry period in summer 2018, the next dry out events occurred in summer as well as in autumn 2018 and two flush events were investigated in October and December 2018. The chemical changes of the spring water due to extreme weather events are compared to other springs of the Upper Harz Mountains and are discussed in Bozau et al. (2021).

The intensified measurements started in March 2020. Data (pH value and SEC) were recorded almost once a week in the spring water and the nearby lake "Entensumpf". The SEC data [μS/cm] for the spring and lake water are compared to daily precipitation [mm] and are shown in Fig. 2 for the years 2020–2023.

Precipitation data for the nearby DWD observation station at Braunlage were taken from the website of the WetterKontor GmbH (www.wetterkontor.de). The distance of the DWD station at Braunlage (607 m a.s.l) to the spring (614 m a.s.l) is about 20 km. SEC and pH were measured with a conductivity meter (WTW cond 3310, TetraCon measure cells) and a pH meter (WTW pH 3110, Sentix electrodes) directly at the spring outflow and within the lake. The field measurements took place at defined points of the spring and the lake. All persons involved in the measurements were carefully incorporated. Selected water samples were titrated with HCl to calculate the bicarbonate concentration and analysed for major ions by ion chromatography as described in Bozau et al. (2013). The titration was done in our laboratory directly after

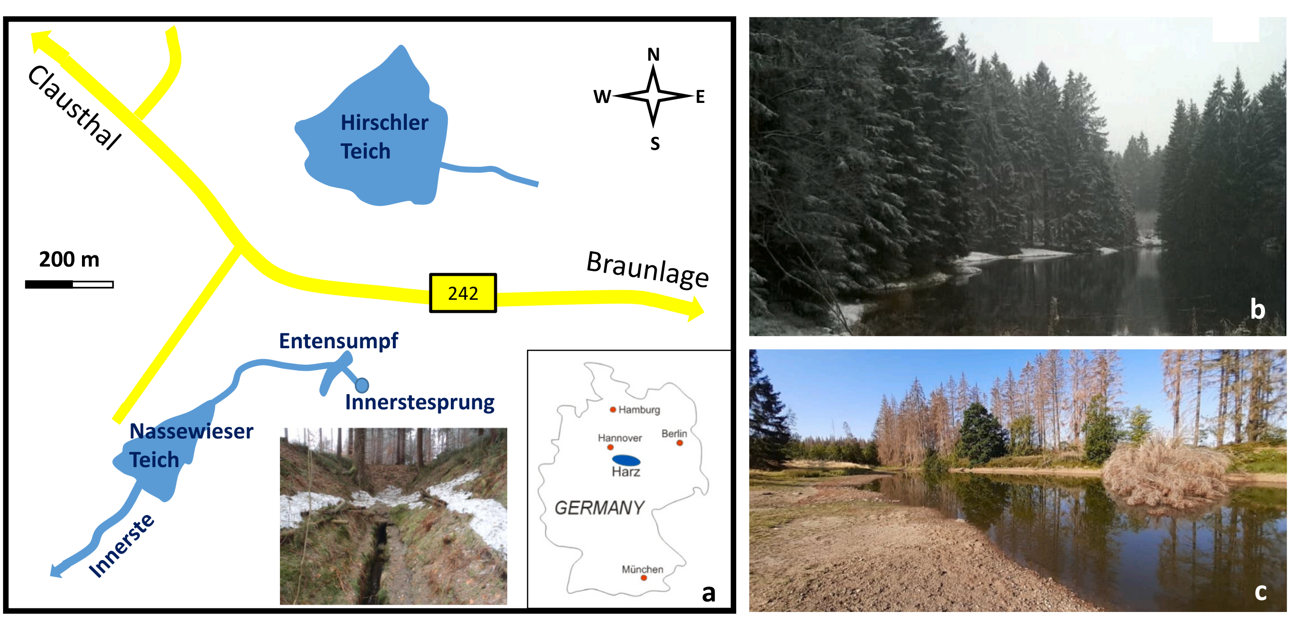

Fig. 1. Study area of the spring "Innerstesprung" (51°47'16.5″N, 10°22'11.7″E) and the lake "Entensumpf" near Clausthal-Zellerfeld in the Harz Mountains (Germany)
Schematic sketch including a picture of the spring's outflow channel (a), view of the lake "Entensumpf" in December 2018 (b) and in August 2022 (c).

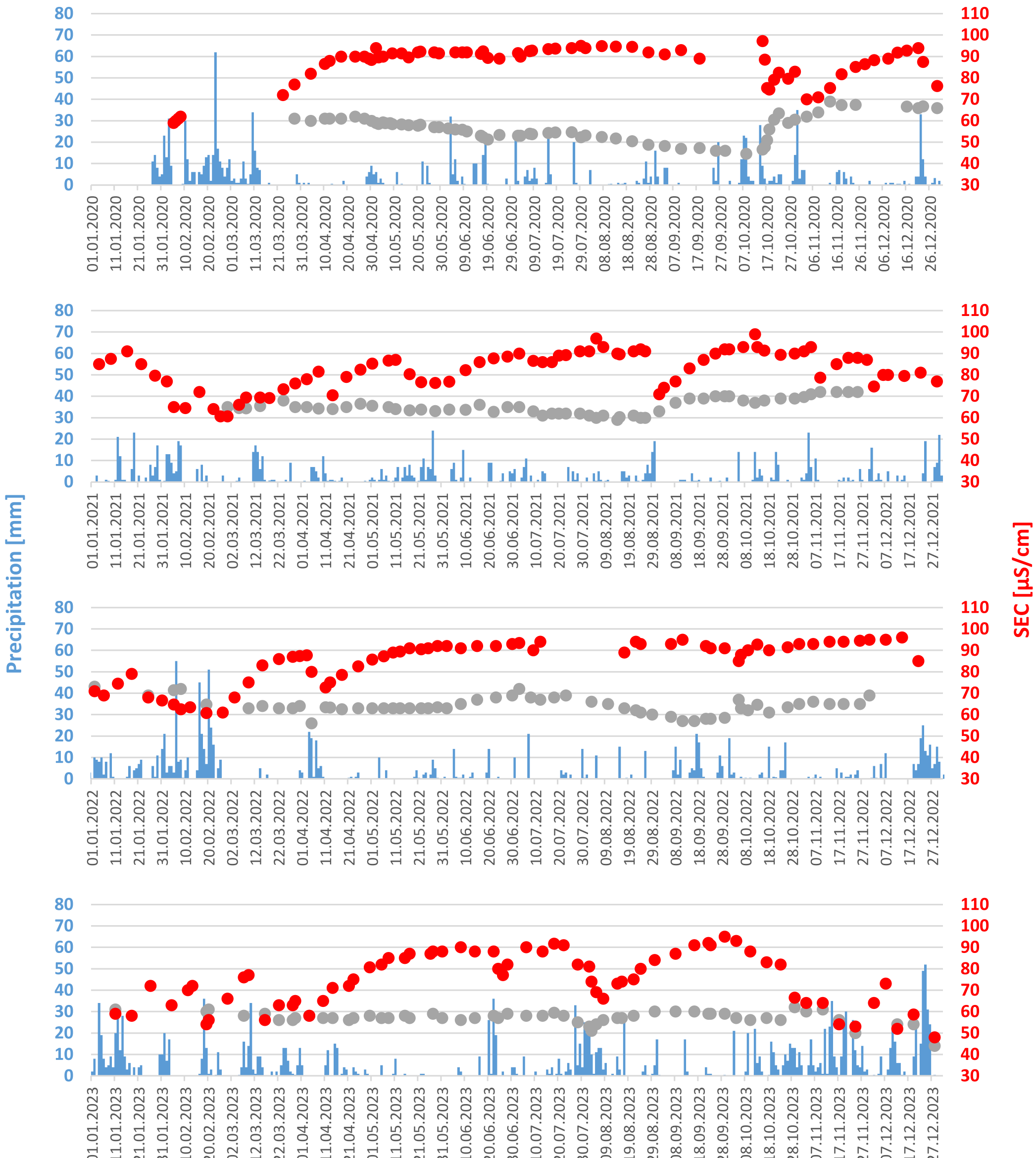

Fig. 2. Daily precipitation (blue columns) and weekly SEC data for the spring (Innerstesprung, red dots) and the nearby lake (Entensumpf, grey dots) measured 2020–2023.

sampling. An outgassing in the sample bottles was never observed. The concentrations of major ions are discussed in their relation to SEC and shown at the end of the discussion chapter.

To get more information about the water-rock interaction in the study area batch tests have been performed. Greywacke samples were collected in the catchment area of the spring. They were well mixed and ground. Different masses of the resulting powder (4–100 g) were eluted with 1 l deionised water in plastic bottles for more than 2 years. The SEC was regularly measured with the WTW conductivity meter 3310 in adapted time intervals.

3. Results and discussion

As known from hydrogeochemical investigations (Bozau et al., 2021) there is a typical SEC range for each individual spring in the Harz Mountains. This range depends on the flow regime, in particular the residence time and flow pathways/tubes in the specific catchment area. The spring of the river "Innerste" consists of one flow tube and shows a quick response to changing precipitation events. Compared to nearby springs, the spring "Innerstesprung" dries out first and after sufficient precipitation it is the first spring starting to flow again (Bozau et al., 2021). The spring "Innerstesprung" is flowing into the nearby lake "Entensumpf". This little lake receives its water from the spring and from precipitation. The water temperature of the lake follows the seasonal air temperature, whereas the temperature range of the spring water is much smaller due to the more stable water temperature in the aquifer (Mattheß, 1994; Benz et al., 2017). There are less data for the lake water because it was often frozen in wintertime whereas the spring water was continuously flowing.

The SEC data for the years 2020–2023 are shown in Fig. 2 and will be discussed for each year. A summary of yearly precipitation, pH and SEC data is given in Table 1.

3.1. *Annual course of precipitation and SEC*

3.1.1. *2020*

The measurement started in early February. Heavy storm events with high precipitation rates interrupted the data collection because it was too dangerous for walking through the forested areas around the spring. In March, parallel to the Corona lockdown, the measurements were

Table 1
Annual precipitation of the nearby DWD observation station, pH and SEC range of the spring and observed drying out events (n = number of water samples, *Not all daily precipitation data were measured at the DWD station. **Minimal value measured on December 28th, 2023.)

Year	Precipitation [mm]	n	pH Min … Max	SEC [μS/cm] Min … ø … Max	Drying out
2010	1054	36	5.4 … 7.3	57 … 78 … 98	–
2011	1054				–
2012	1142				–
2013	1127				–
2014	1142				–
2015	1313				–
2016	1045				September–October
2017	1591				–
2018	913				August–October/November
2019	1228				–
2020	1209	68	5.9 … 6.6	60 … 88 … 97	September–October
2021	932	73	5.3 … 6.7	61 … 83 … 99	–
2022	1099	61	5.4 … 7.4	61 … 85 … 96	July–August/September
2023	1760*	65	5.3 … 6.9	48**/52 … 75 … 93	–

resumed. The SEC value was rising continuously up to about 90 μS/cm in April. Then the precipitation was not high enough to lower this value. In September, the spring dried out. Two following precipitation events did not deliver enough water. Only, a third precipitation event with 37 mm rain within two days (October, 14th and 15th) was able to flush the spring. This first flush event is reflected in the highest SEC values of 97 μS/cm measured in 2020. Such high SEC values are typical for first flush events because the time for water-rock interaction in the catchment is longer during dry periods leading to a higher mineralisation of the water. Up to the end of the year, the SEC of the spring water was rising with two interruptions by higher precipitation events. The SEC of lake water was decreasing from April until the first flush event of the spring in October. This can be explained by a decreased inflow of spring water and the influence of rain water with very low SEC values falling directly on the water surface of the lake. The flush of the spring leads to higher SEC values in the lake. In November the lake was frozen so that the SEC could be measured only in the spring water.

In December 2020, the spruce forest of the spring catchment was cleared by the forest holding company.

3.1.2. 2021

The new year 2021 started with much snowfall leading to a thick snow and ice cover in the catchment area. Because of the frozen cover recharge could not reach the spring and the SEC of the spring water was rising. The nearby lake was frozen until the end of February. Later, the thawing water slowly filled the fractured rocks of the catchment area. Although the annual precipitation amount was low, the slow recharge after snowmelt and continuous rain events were able to sustain the spring flow during summer and autumn. There was a quite strong rain event at the end of August (33 mm precipitation on August, 29th and 30th) lowering the SEC value from 90 to 70 μS/cm. The lake was frozen from the end of November up to January 2022.

3.1.3. 2022

Snowfall in January was lower than in 2021. The storms in February were comparable to 2020. Measurements in February were possible because the spruce trees were cut. The precipitation amounts in springtime were low and the runoff of the spring water strongly decreased in June. Dry out started at the beginning of July. Compared to the dry out processes in 2018 and 2020 where no water was seen at the spring outflow, little puddles with dammed-up waters developed. The SEC of the puddle water was measured in August and September. Distinct flow from the spring to the lake started at the end of September. The precipitation amount which initiated the flow was about 40 mm. SEC values higher than 95 μS/cm known from first flush events of 2018 and 2020 were not reached. The water level of the lake “Entensumpf” was very low (Fig. 1). Snowfall started in November. But first, the heavy rain events in December led to a decrease in SEC values of the spring water.

The vegetation of the catchment area recovered. The spruce vegetation changed to mountain ash and blackberry bushes.

3.1.4. 2023

This year is characterised by well distributed monthly precipitation events. Even in June and July, precipitation led to a decrease in the SEC of the spring water. The precipitation amounts from October up to December were extremely high compared to the normal variation of precipitation in the study area. Therefore, the typical correlation of high precipitation leading to low SEC values of the spring water was seen in all seasons.

There was an extremely high precipitation rate in December 2023. 200 mm of precipitation falling as rain were noted from December 20th to 26th at the nearby weather station. This led to a flooding of the area at the spring outflow. The SEC of 48 μS/cm measured on December 28th is the lowest value found during the monitoring time. The surface water of the lake “Entensumpf” had an SEC of 44 μS/cm at this time. Its water level was very high and prevented a continuous inflow of the spring water. Because of a possible mixing between rain water, surface runoff, lake, and spring water at the observation point it is not certain if such a minimal value can be derived only from the outflow of the spring water.

3.2. Runoff and SEC

According to the observations from 2010 to 2023, a precipitation amount of about 40 mm within 2 days is needed to flush the spring “Innerstesprung” after drying out. Baseflow characteristics and the prediction of drying out aquifers and springs are important questions in hydrological research (Dewandel et al., 2003). A hysteretic relationship between runoff and chemical water composition is often observed in various catchments (e.g., Butturini et al., 2005; Engel et al., 2019). The exponential equation of Maillet (1905), also known as hydrological recession curve, with the runoff Q, the initial runoff Q_0, the time t and a catchment specific coefficient a

$$Q = Q_0\, e^{-at}$$

is helpful to estimate decreasing runoff and understand the flow regime of different catchment areas. Due to its simplicity this equation is widely used in hydrology (Collignon, 2021) and can be applied to the corresponding SEC data for the “Innerstesprung” which show the inverse behaviour compared to Q:

$$SEC = SEC_0\, e^{at}$$

Evaluating the measured SEC data given in Fig. 3 for long periods without precipitation, the coefficient a for SEC in μS/cm and t in days is

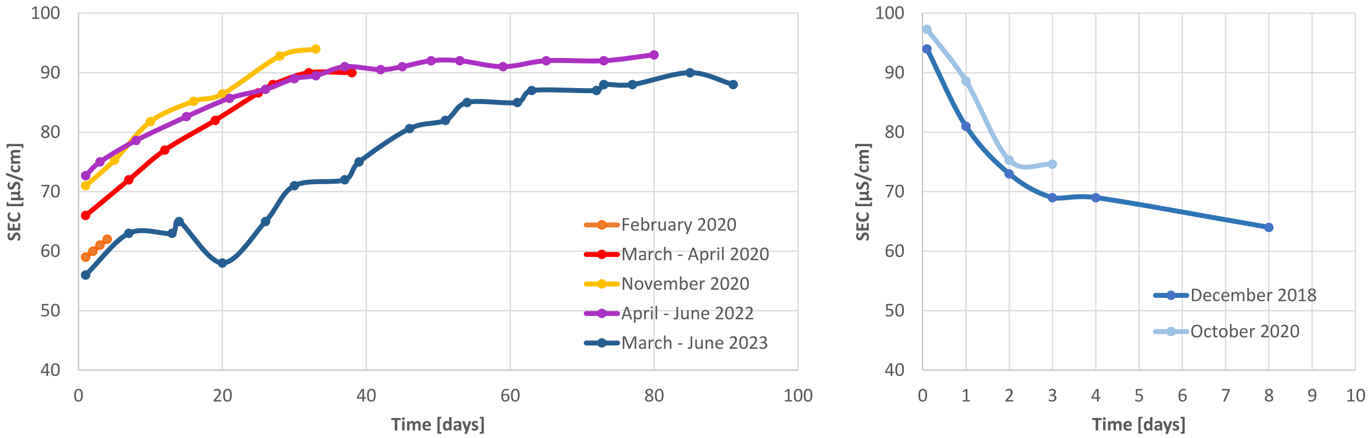

Fig. 3. SEC changes during days without or almost no recharge/precipitation (left) and flushing events of the spring after drying out (right).

about 0.009. The variations of the coefficient *a* can be explained by the weather conditions during the measurements. During dry periods SEC is continuously rising (e.g., April – June 2022) ending up in the drying out of the spring water. But such a rise in SEC can be interrupted by one heavy rain event only (e.g., April 2023) leading to a decrease of SEC, and the beginning of the next dry period (e.g., March – June 2023). A further scenario when moderate precipitation amounts sustain a low, but continuous flow of spring water, results in almost stable SEC values higher than 90 µS/cm for a long time before drying out (e.g., March – September 2020).

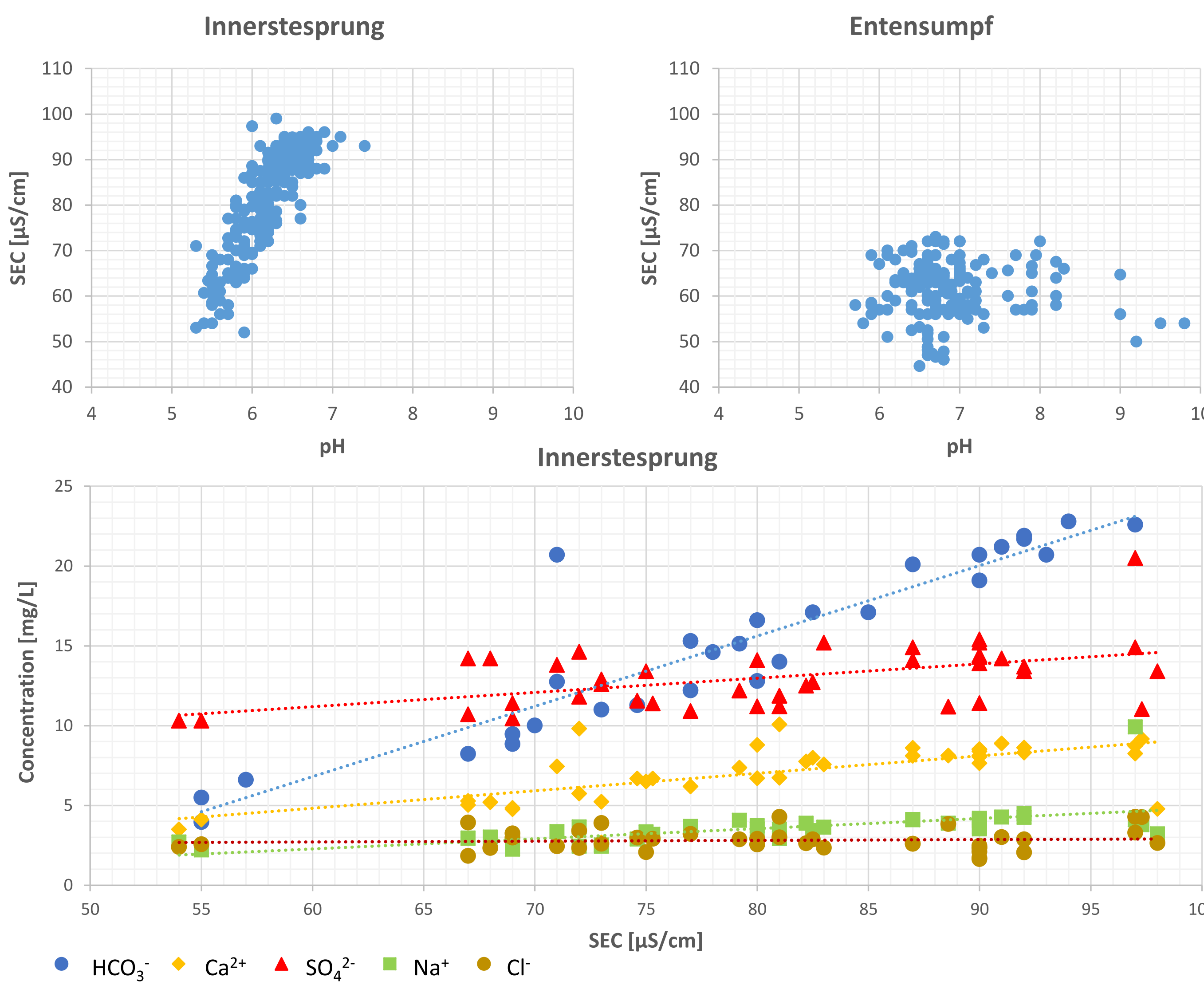

Fig. 4. Correlation plots, pH vs SEC for the spring and lake water (above) and SEC vs main ions for the spring water (below).

The SEC behaviour during long periods with frozen snow cover (e.g., January 2021) is comparable to dry periods because the recharge in the catchment area is also reduced. A slow snowmelt in springtime with reduced surface runoff allows a continuous recharge to the aquifers.

3.3. Chemical characteristics of the spring water

SEC and pH of the spring "Innerstesprung" are well correlated whereas no trend for SEC and pH is seen in the lake "Entensumpf" (Fig. 4). The spring water reflects the pH and SEC correlation of the rain water. High precipitation amounts lead to lower pH values and ion concentrations due to atmospheric wash out effects. The lake receives its water from the inflow of the spring plus rain water. But limnological processes overthrow the input pattern especially in summertime when biological activity is high (Maberly, 1996; Xie, 2006).

Increasing SEC in the spring water correlates with increasing concentrations of bicarbonate and calcium and slightly increasing concentrations of sodium. Compared to the other ions the high bicarbonate concentrations attract attention, especially because the fractured aquifer is composed of shales and greywackes which have only accessory carbonate minerals. The $\delta^{13}C$ values for bicarbonate are about −20 ‰ in the spring water. Comparable values are found in neighbouring springs of the Harz Mountains (Bozau et al., 2023). Such isotope values indicate that the main source of dissolved inorganic carbon is CO_2 originating from root respiration and the degradation of C3 organic matter in the soil zone (Spence and Telmer, 2005; Boutton et al., 1998). Studies in watersheds consisting of non-carbonate rocks (e.g., Nordstrom et al., 1992) also reveal that the dominant process for bicarbonate formation is the production of carbon dioxide in the soil zone through aerobic decay of organic matter. The source for calcium and sodium is likely the weathering of silicate minerals of the soil zone and the surrounding rocks. Almost stable concentrations are found for sulphate and chloride, a possible indication for atmospheric inputs slightly added by the decay of organic material.

A batch test with greywacke of the study area was performed. Different rock masses are eluted with deionised water. The SEC values have been measured for 2 years to reach chemical equilibrium conditions (Fig. 5). The change of SEC values should be comparable to the data given in Fig. 3 for drying out events at the spring. Therefore, the SEC values of the spring water during dry periods are also inserted in Fig. 5. An SEC increase of spring water from about 70 μS/cm to 95 μS/cm within 30 days is found in 2020 and 2022. But these time dependent SEC changes seen at the spring are higher than the changes in the batch test for about 30 days. Later, the SEC values at the spring are constant whereas the values of the batch tests are still rising. Comparing the SEC ranges of the batch tests and the monitored data at the spring, it is not possible to explain the SEC values of the spring water alone by the elution behaviour of greywacke. There are two further sources for the mineralisation of the spring water: the seasonal changing chemical composition of the rain water and the enrichment of the SEC during recharge processes in the soil and in the rocks above the aquifer. The microbiological processes of the soil zone seem to be a very important source of dissolved ions in the spring water as already discussed above for the bicarbonate concentrations. Furthermore, the processes of water-rock interaction at the flow path of the spring water in the aquifer differ from the conditions during the batch tests. The formation of secondary minerals at the flow path can reduce the elution of primary minerals forming the aquifer rocks (e.g., Locsey et al., 2012). Evaluating the results of the batch tests it is only possible to state that a mixing ratio of less than 40 g greywacke in 1 l deionised water leads to SEC values lower than 100 μS/cm as observed for the water of the spring "Innerstesprung".

4. Conclusions

SEC data of the spring "Innerstesprung" can be used to characterise the runoff volume. There is a specific relationship of precipitation, runoff and SEC for the spring. Comparing SEC data and major ion concentrations of the spring water typical trends attributed to different processes (e.g., bicarbonate: degradation of organic matter in the oil zone, calcium and sodium: silicate weathering) in the catchment area can be seen. Changes in runoff and chemical water composition due to forest decline and vegetation changes cannot be attested by the investigated parameters. During the observation period (2010–2023), an increase of the drying out frequency was evident for the spring "Innerstesprung" since 2016. Drying out of spring water always depends on the actual precipitation rate and the recharge behaviour of the catchment area. Therefore, a correct long-term weather forecast for the specific catchment area is needed. According to meteorological processes in the Earth's atmosphere there is a very high uncertainty for regional

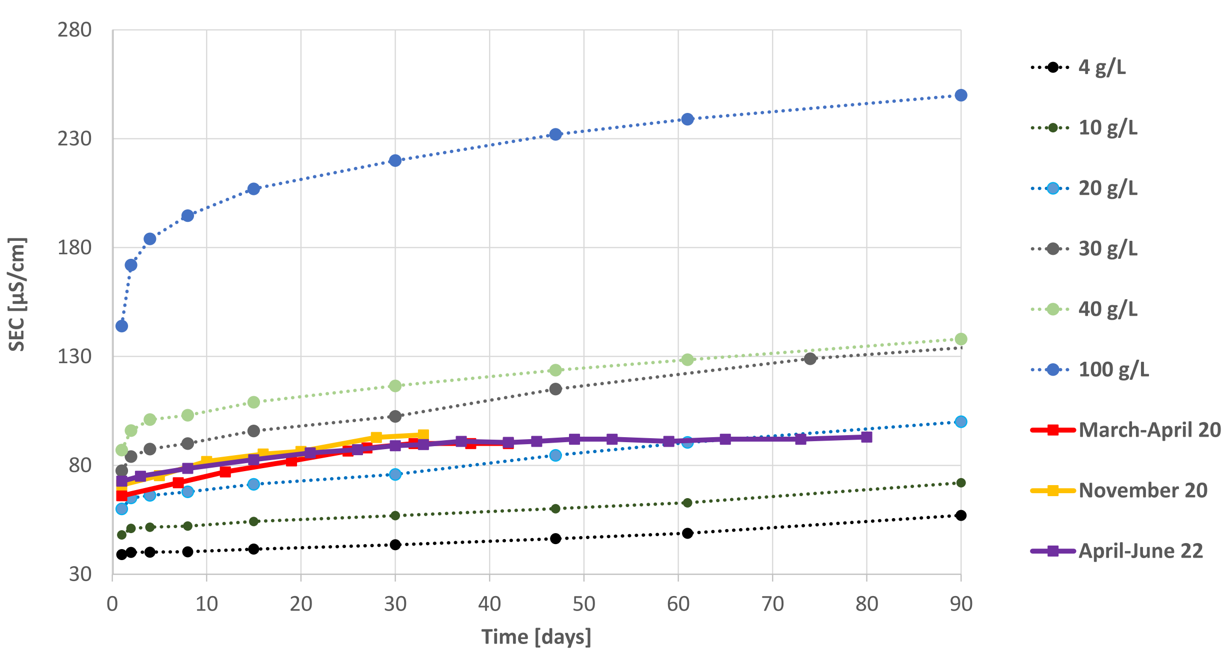

Fig. 5. SEC development during batch tests with greywacke for different rock-water mixing ratios compared to field data of SEC during dry periods.

predictions. The reliability of meteorological predictions for 3 days is estimated to be about 75 %. This dependence on meteorological prognosis does not allow a correct prediction of drying out events for the springs in the Upper Harz Mountains. But, based on the monitoring data the minimal amount of precipitation to flush the spring "Innerstesprung" is known. A precipitation amount of about 40 mm is needed to flush the spring of the Innerste river after drying out events.

The characterisation of subsurface watersheds in fractured rocks of forested mountain ranges is always challenging. SEC measurements cannot replace the necessary hydrodynamic and hydrochemical investigations, but SEC data are time and cost efficient parameters to monitor the runoff and hydrochemical trends in spring watersheds. After a careful hydrological investigation of the catchment area, a monitoring concept based on SEC data can be developed and easily realised. If unexpected SEC values are measured in a watershed, further investigations to check the cause must be carried out. But as shown for the spring of the Innerste river, valuable hydro(*geo*)logical information can be drawn by continuous SEC measurements.

CRediT authorship contribution statement

Elke Bozau: Writing – original draft, Supervision, Project administration, Methodology, Data curation, Conceptualisation. **Tanja Schäfer:** Writing – review & editing, Validation, Data curation. **Tobias Licha:** Writing – review & editing, Resources, Methodology, Conceptualisation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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