

Water quality and water-rock interaction in the Harz Mountains (Germany)

Elke Bozau*, Hans-Joachim Stärk**, Gerhard Strauch***, Claudia Swanson****

*TU Clausthal, Endlagerforschung, Leibnizstraße 10, 38678 Clausthal-Zellerfeld (elke.bozau@tu-clausthal.de)

**Helmholtz-Zentrum für Umweltforschung (UFZ), Analytik, Permoserstraße 15, 04318 Leipzig

***Helmholtz-Zentrum für Umweltforschung (UFZ), Hydrogeologie, Permoserstraße 15, 04318 Leipzig

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Abstract. The Harz Mountains, known for ancient silver and base metal mining, are an important drinking water supply region for northern Germany today. The water quality of the Harz Mountains is mainly influenced by atmospheric deposition, water-rock interaction and biological activities. Anthropogenic influences are minor. Springs, creeks, lakes and reservoirs have a relatively low mineralisation. Measured as specific electrical conductivity (SEC), the mineralisation of the different water bodies ranges from about 15 to 650 $\mu\text{S}/\text{cm}$. Only deep springs and mine waters reach higher values. Despite of dilution effects due to different rain water amounts, water-rock interaction can be retraced by the chemical water composition, especially by trace metals and Rare Earth Element (REE) concentrations. Examples of water-rock interaction are discussed for granite (lake Oderteich), greywacke/schist/siltstone (Rammelsberg mine), and limestone (lake Blauer See).

1. Introduction

Transport and geochemical modelling in drainage basins is based on the understanding of water-rock interactions that include many natural geochemical processes like weathering, dilution, precipitation and sorption, as well as microbiological interactions and anthropogenic influences (Oelkers & Schott, 2009). These basic processes can be easily studied in mountains ranges where surface waters (e.g., lakes, reservoirs and springs) are situated in relatively small drainage basins with well-known rock compositions and low anthropogenic impacts.

Mountain catchments in Germany are characterised by high precipitation rates and surface water runoff. Surface waters from these catchments are often stored in water supply dam reservoirs. The Harz Mountains are an important drinking water supply region for northern and eastern Germany today. Hydrogeochemical studies in this area with special focus on spring water quality, nitrogen dynamics and atmospheric inputs have been performed for a long time (e.g., Aliche, 1974, Matschullat et al., 1994, Frei et al., 2000, Plessow et al., 2001, Bozau et al., 2013, Mueller et al., 2015). Long term measurements are also done by the companies which are responsible for reservoirs in the Harz Mountains and the drinking water supply (e.g., Lange et al., 2010, Mehling et al., 2012). In this study, we try to combine the data of several studies to understand main hydrogeochemical processes, especially water-rock interaction in the different geological units of the Harz Mountains. General explanations of water-rock interaction are given. Geochemical details, e.g. REE and trace metal concentrations, are discussed. It is tried to find typical geochemical indicators for water interaction with rocks like granite, limestone and greywacke.

2. Study area

The Harz Mountains, situated in the north of Germany, are about 120 km long and about 40 km broad. The highest mountain is Mount Brocken with 1141 m a.s.l., a granite pluton dated of about 283 Million years (Zech et al., 2010). The mountain range consists of Palaeozoic rocks which can be divided in several regional geological units (Bachmann et al., 2008). Most of upcoming the rocks have a low permeability causing a strong discharge at the surface, soil and weathering zone (Jordan & Weder, 1995). Therefore, there are frequently found springs connected to different rock layers and fractures. Aquifers are not well developed and are of minor importance for water use.

The precipitation rate is increasing with altitude. At the highest elevations (700 up to 1100 m a.s.l.) mean annual precipitation rates range between 1400 up to 1800 mm. The watershed between the two river systems Elbe and Weser crosses the Harz Mountains.

Acid rain and atmospheric deposition in the Harz Mountains led to increased metal mobility in soils and metal concentrations in drainage water. Detailed effects of air pollution are discussed in several studies (e.g., Andreae, 1993; Matschullat et al., 1994; Roostai, 1997). According to air pollution control measures, the ecosystem starts to recover. This effect can be seen as decrease of sulphate concentrations in springs (Bozau et al. 2013).

Because of several yielding mineralisations, mining activities in the Harz Mountains have a long history. Mining is thought to be started already in the Bronze Age (Matschullat et al., 1997) and has been wide spread since the Middle Ages (Ließmann, 1992; Klappauf, 1994). Those mining activities have consequently caused contaminations of surface waters as well recharge areas. But the majority of waters is chemically not affected by mining. Most of them are involved in the "Oberharzer Wasserregal", which is an old system of dams, adits, reservoirs and ditches. It was constructed from the 16th to 19th centuries to deliver water to the water wheels of the mines mainly situated around the towns of Clausthal-Zellerfeld, Sankt Andreasberg and Altenau. As a historic mining management system the "Oberharzer Wasserregal" was declared an UNESCO World Heritage Site in 2010. The museum of the Rammelsberg mine and the historic town Goslar also belong to this World Heritage Site.

Reservoirs (e.g. Innerste-, Rappbode-, Oker-Stausee) for flood protection, energy production and drinking water supply were built in the 20th century. An amount of about $70 \cdot 10^6 \text{ m}^3$ high quality water per year from these reservoirs is delivered to several users (Müller, 1991). The biggest reservoir of the Harz Mountains is reservoir "Rappbode-Stausee" with a total water volume of $109 \cdot 10^6 \text{ m}^3$. The 6 big reservoirs of the western Harz Mountains (Ecker-, Innerste-, Grane-, Oder-, Oker-, Söse-Stausee) have a water storage capacity of $182 \cdot 10^6 \text{ m}^3$ and are controlled by the company Harzwasserwerke which is also responsible for the water management system "Oberharzer Wasserregal". The water volume of the lakes involved in the "Oberharzer Wasserregal" is estimated of about $12 \cdot 10^6 \text{ m}^3$. So the volume of about $200 \cdot 10^6 \text{ m}^3$ can be considered as the minimum volume of surface runoff leaving the western part of the mountain range. Involving meteorological data and recharge calculations (Lemke & Elbracht, 2008) the surface water volume leaving this part of the Harz Mountains can reach to about $400 \cdot 10^6 \text{ m}^3/\text{year}$. Investigations of the company Harzwasserwerke in the drainage basins of the reservoirs and further creeks show that the annual water runoff is nearly constant since 1941 when the measurement started. But the seasonal runoff volume is changing. Summer time is getting dryer resulting in lower runoff whereas during winter time runoff volumes from the Harz Mountains are rising (Lange, 2012).

Deep thermal springs near Bad Suderode and Bad Harzburg at the north boundary of the Harz Mountains are in contact to Mesozoic rock. They are used for balneo-therapeutical purposes. According to their main anions Na or Na and Ca the deep springs can be related to upper Triassic rock or lower Triassic rocks (Buntsandstein) and Permian layers. More information about these springs is given in Bozau & van Berk (2014) and in Kübeck (2004).

3. Water Sampling

Water samples of the Harz Mountains are taken regularly during student excursions and for different scientific projects by all authors of this study. The samplings started in 2010 and span all seasons. To show the effects of water-rock interaction, data of several sampling campaigns are combined in this study (Table 1).

Generally, pH, temperature and specific electrical conductivity are measured during sampling. The main ions are analysed after $0.45 \mu\text{m}$ filtration by ion chromatography, trace elements and rare earth elements are determined by ICP-MS. For further analytical details see Bozau et al. (2013).

Table 1: Hydrogeochemical characteristics (pH value, specific electrical conductivity and main ions) of waters in the Harz Mountains

	Sampling date (Sampling number)	pH	SEC μS/cm	Na ⁺ mg/l	K ⁺ mg/l	Ca ²⁺ mg/l	Mg ²⁺ mg/l	SO ₄ ²⁻ mg/l	Cl ⁻ mg/l
Rain water Clausthal-Zellerfeld*	2013-2014 (n=35)	4.4-6.8	5-43	<0.05-1.6	<0.05-1.2	<0.05-2.0	<0.05-0.20	0.32-3.3	0.06-3.4
Lake "Oderteich" near Mount Brocken	2013 (n=1) 2015 (n=1)	4.6 4.7	59 58	6.0	0.9	1.6	0.5	3.7	9.2
Lake "Blauer See" near Elbingerode	2015 (n=1)	9.9	330	7.6	1.8	34	0.7	37	15
Spring "Bode"*** near Mount Brocken	2010-2012 (n=4)	4.2-7.5	16-43	0.8-1.4	0.1-0.8	0.3-4.3	0.1-0.9	0.7-1.1	0.5-1.7
Creek "Bode" at Treseburg and Neinstedt leaving the Harz Mountains	2015 (n=1) 2015 (n=1)	7.8 7.8	200 240	12	1.4	25	3.2	12	22
Spring "Innerste"*** near Clausthal-Zellerfeld	2010-2014 (n=14)	5.8-7.3	63-97	3.0-9.9	0.5-1.2	5.2-9.8	1.4-2.8	13-21	1.6-4.3
Creek "Innerste" at Langelsheim leaving the Harz Mountains	2014 (n=1)	8.1	191	12	1.2	21	3.9	26	33
River "Innerste" at Hildesheim (about 40 km away from the Harz Mountains)	2012 (n=1) 2014 (n=1)	8.1 8.1	825 840	64 57	5.2 4.9	126 81	15 12	115 96	104 96
Reservoir "Innerste-Stausee"	2012 (n=1)*** 2014 (n=1)	7.7 8.2	160 172	9.9	1.1	19	3.5	23	13
Spring "Eisenquelle" near Clausthal-Zellerfeld	1972-1973****(n=7) 2010-2015**(n=6)	5.1-6.5 5.0-7.8	61-94 73-115	5.8-8.1 7.6-10	1.8-2.3 0.5-1.1	2.3-4.0 3.3-8.0	2.6-3.2 1.5-3.3	8.0-28 5.5-8.4	4.9-14.3 7.1-17.5
Mine water "Rammelsberg" near Goslar	2013 (n=1)	6.5	1870	48	9.0	313	95	1100	38
Deep springs (North of Harz Mountains)									
Bad Harzburg*****	2003 (n=1)	7.6	34700	7523	115	1138	200	3845	11200
Bad Suderode*****	2001 (n=1)	7.5	26500	3835	60	2560	4.6	16	9320

*Bozau et al. (2015)

**Bozau et al. (2013)

***Mehling et al. (2012)

****Alicke (1974)

*****Kübeck (2004)

4. Water quality and water-rock interaction

To characterise the water-rock interaction and its influence on the water quality, three main geological units of the Harz Mountains are considered (Figure 1):

- granite of the Upper Harz around the Mount Brocken,
- limestone of the unit "Elbingröder Komplex" in the Middle Harz,
- greywacke, schist and siltstone.

The mineralisation of the waters from all these areas is relatively low. Some springs and lakes are characterised by ion concentrations not higher than rain water. Measured as specific electrical conductivity (SEC), the mineralisation of the different water bodies ranges from about 15 to 650 $\mu\text{S}/\text{cm}$ (Figure 2). The springs formed in the granitic region of the upper mountains with higher precipitation rates have lower SEC values than the springs of the lower areas dominated by greywacke and schist according to the lower rain water dilution. Only deep springs (e.g., at Bad Harzburg and Bad Suderode) and mine waters (Rammelsberg mine near Goslar) reach values $> 1,000$ $\mu\text{S}/\text{cm}$. These values are still lower than sea water mineralisation and can be explained by intensive water-rock interaction with the surrounding Mesozoic rocks at the northern boundary of the Harz Mountains and the exploited ore minerals, respectively.

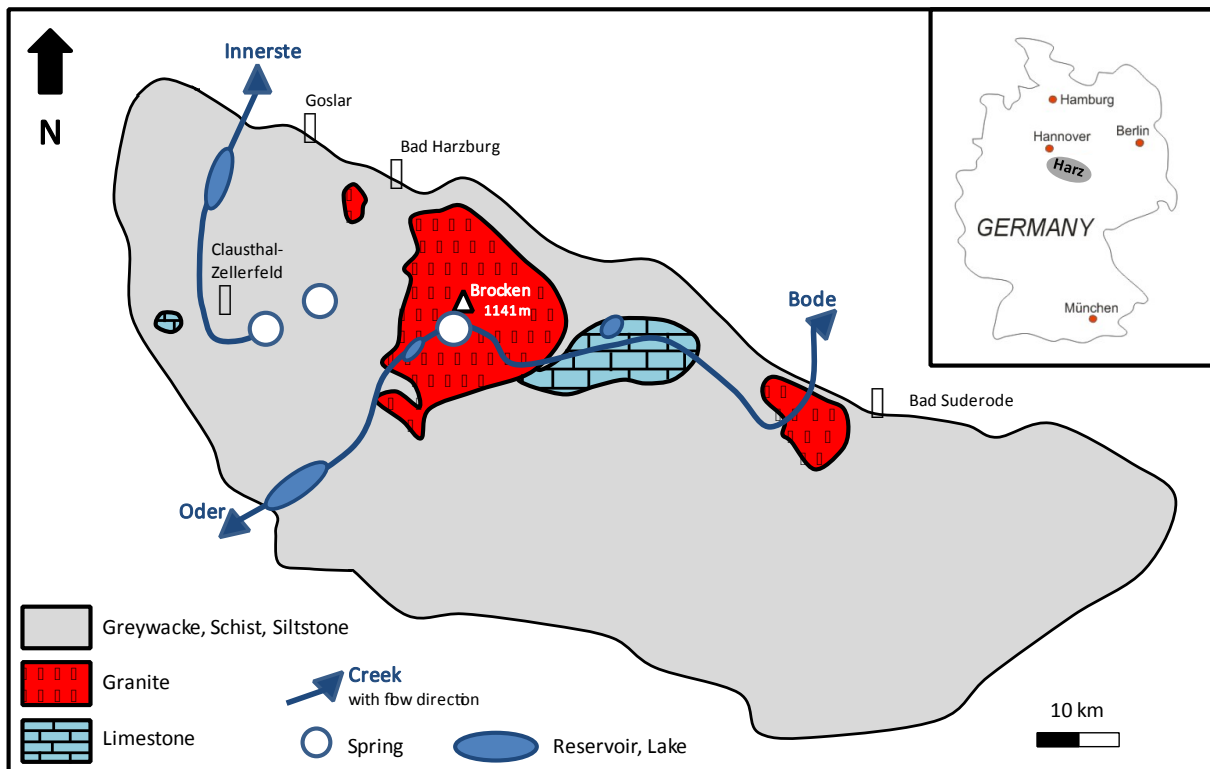


Figure 1: Simplified sketch of the Harz Mountains with the considered rock units and the sampling locations of this study - springs (Innerste, Eisenquelle, Oder, Bode), creeks (Innerste, Oder, Bode), lakes (Oderteich, Blauer See) and reservoirs (Innerste-Stausee, Oder-Stausee)

For detailed geographical and geological information of the Harz Mountains see:
<http://www.geopark-harz.de/>.

Despite of dilution effects due to different rain water amounts, water-rock interaction can be retraced by the chemical water composition in all investigated waters. Seasonal changes are observed especially in spring waters. Some springs around Mount Brocken which are strongly

depending on surface water supply can dry out in summer or are frozen in winter time. These springs are also characterised by a high amount of organic materials measured as DOC originated by the numerous peat bogs in this area (Bozau et al., 2013). The investigated creeks (Table 2) show an increase of ion concentrations downstream due to rising biological activities and further water-rock interactions. The highest concentration in the creeks is measured when they are leaving the mountain range (Table 2). The SEC of the creek “Innerste” is rising from 87 $\mu\text{S}/\text{cm}$ at the spring up to 191 $\mu\text{S}/\text{cm}$ at the boundary of the Harz Mountains in Langelsheim. In Hildesheim, 40 km away from the mountains, a SEC value of about 820 $\mu\text{S}/\text{cm}$ is measured in the river “Innerste”. The creeks “Bode” and “Oder” leave the Harz Mountains with a SEC of about 200 and 100 $\mu\text{S}/\text{cm}$, respectively.

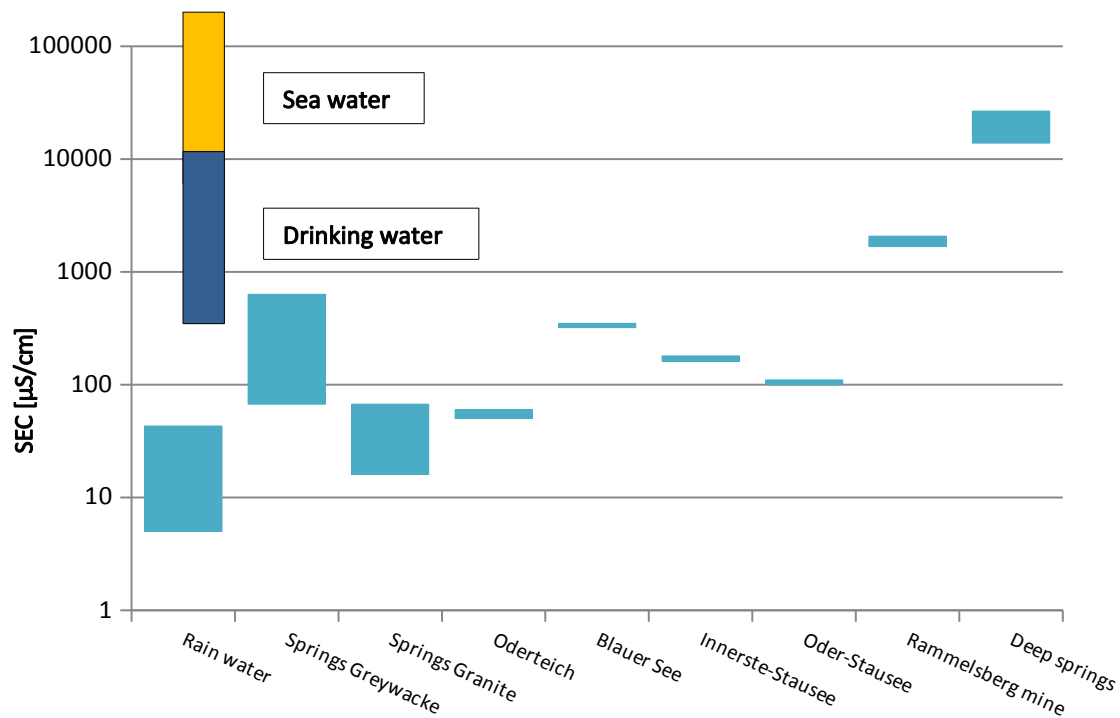


Figure 2: Specific electrical conductivities measured in waters of the Harz Mountains, sea water (52.000 $\mu\text{S}/\text{cm}$) and the German threshold value for drinking water (2.500 $\mu\text{S}/\text{cm}$). Data of rain water and springs are from Bozau et al. (2015 and 2013) and data of deep springs are from Kübeck (2004).

Table 2: Specific electrical conductivity of the creeks “Innerste“, “Bode“ and “Oder“ from the spring downstream

Innerste September 2014	SEC $\mu\text{S}/\text{cm}$	Bode June 2015	SEC $\mu\text{S}/\text{cm}$	Oder July 2013	SEC $\mu\text{S}/\text{cm}$
Spring	87	Spring	dry	Spring	35
Wildemann 12 km	145	Elend 10 km	60	Oderteich 4 km	59
Reservoir 25 km	173	Treseburg 38 km	200	Inflow Reservoir $\frac{1}{2}$ 19 km	94/117
Langelsheim 30 km	191	Neinstedt 50 km	240	Reservoir 22 km	106

According to the high rain water amount and the low ion concentrations of rain water, water-rock interaction of the considered rock units will be better seen in the minor and trace element

concentrations deriving from rock minerals than in the concentrations of the main elements. If trace elements are detected in spring water they must originate from the soil or rock, because trace element concentrations of the rain water are very low and often below the detection limits for trace elements. Therefore, trace metals and Rare Earth Elements (REE) are useful tracers of water-rock interaction.

Some of the major rain water ions, e.g. NH_4^+ are already degraded within the soil zone. The average rain water concentration of NH_4^+ is 0.9 mg/l (Bozau et al., 2015), but NH_4^+ is not detected in the spring water. According to the biological processes within the soil zone, organic matter is degraded and the CO_2 content is rising changing the ratios of the main ions from the rain water, too.

Water in contact with a rock will equilibrate with the minerals of that rock. The main minerals of granite are quartz, feldspar minerals and micas. Greywacke, schist and siltstone consist mainly of quartz and clay minerals. Calcite is the main component of limestone. The dissolution of calcite will increase the pH value of water faster than biological activities in the soil zone and the water bodies. Surface water will also equilibrate with the oxygen and carbon dioxide content of the atmosphere. Waters of the ore mines are influenced by the dissolution of ore and secondary ore minerals. These waters can be enriched in metals and if sulphide minerals are weathered under oxygen supply, the sulphate contents will rise. Combined with the precipitation of iron oxyhydroxides, this process can lead to the formation of acid mine drainage.

Table 3: Minor and trace elements of waters from different geological units

Rocks	Granite				Greywacke, schist, siltstone			Limestone
Sample	Spring Bode	Spring Eule	Creek Oder	Lake Oderteich	Oder-Stausee Inflow 1/2	Spring Innerste	Mine Rammelsberg	Lake Blauer See
Date	Spring 2013	Spring 2013	Summer 2013	Summer 2013	Summer2013	Spring 2013	Autumn 2013	Spring 2015
Al [µg/L]	121	244	228	235	34/19	36	n.a.	28
Fe	121	10	710	845	213/16	5	4	9
Mn	10	73	29	82	60/3	11	12	0.4
Cd [µg/L]	0.09	0.24	0.23	0.21	0.02/0.05	0.19	11	0.003
Cu	1	0.4	4	3	3/3	0.5	35	0.5
Pb	10	3	16	12	2/2	2	<3	0.02
Zn	8	14	12	14	3/14	9	15300	1.1
U	0.026	0.034	0.18	0.14	0.02/0.04	0.009	1	0.002
B [µg/L]	2	2	5	4	9/13	3	140	11
Li	0.13	1.4	1.3	1.2	2.2/1.6	0.81	111	6
Sr	2	4	15	10	23/36	27	2300	66

4.1 Water of the granitic area around Mount Brocken

In the upper parts of the Harz Mountains near Mount Brocken large peat bogs are common and many springs are formed there. The springs of the river „Bode“ and „Oder“ originate in these peat bogs which get most of their nutrients by atmospheric deposition. The water draining the bogs and contacting the weathered granite boulders is rich in organic matter (fulvic and humic acids) and iron. All waters from the granitic area have relatively high Al and Fe concentrations. Compared to the spring “Innerste” (non granitic area) the trace metal concentrations (e.g., Cu, Pb) are also enriched. The highest U concentration (0.2 µg/l) is found in the creek “Oder” (Table 3). The spring “Oder” and some other little creeks feed the lake-reservoir “Oderteich” with a holding capacity of 1.7 Million m³. The lake “Oderteich” as a part of the “Oberharzer Wasserregal” was built in 1722 and is characterised by a very low pH value (about 4.6) combined with high Fe concentrations. The concentrations of the main ions Ca²⁺ and K⁺ are not much higher than the ion concentrations measured in rain water. The sulphate concentration slightly exceeds rain water concentration. If the Na and Cl concentration are can be attributed to the use of road salt is not sure. Acidification due to outflow of peat bog and acid rain found in the upper part of the Mountain range is compensated by buffering processes downstream the creeks.



Figure 3:

- 1) Peat bog near Mount Brocken, origin of the spring “Oder”.
- 2) Sampling at the creek “Oder” that flows around granite boulders.
- 3) Lake “Oderteich” near Torfhaus.
- 4) The red brown water colour refers to the high iron concentrations (Oderteich: up to 1 mg/L).

The REE concentrations and the pattern of the creek “Oder” and the lake “Oderteich” can be attributed to the interaction with the granite that displays the same REE pattern with the typical

negative Eu anomaly and the enrichment of heavy REE. Similar REE patterns are also found in springs from the granitic area (Roostai, 1997; Bozau et al., 2013). The shale normalised REE patterns of the water samples are shown in Figure 4. North American Shale Composite (NASC; Taylor & McLennan, 1985) was used for normalisation.

The outflow of the lake “Oderteich” is leaving the granitic environment, and together with several further creeks it is running into the reservoir “Oder-Stausee”. The construction of this reservoir was finished in 1934 for flood protection. The water is used for energy production. The reservoir as well as many creeks of the western and eastern shore flowing to it are situated in Carboniferous, non granitic rocks. The REE concentrations of the reservoir inflows are lower than that of the lake “Oderteich” and the patterns are flat. The influence of the water coming from the lake “Oderteich” is not seen in the REE pattern of the main inflow shown in Figure 4 and the reservoir. The REE concentrations of the reservoir are lower than the detection limit and therefore not shown in Figure 4. The flat REE pattern and lower REE concentrations are typical for waters from greywacke, schist and siltstone as described in Roostai (1997) and Bozau et al. (2013) and also presented in the next chapter (Figure 5) for the spring “Innerste”. The negative Ce anomaly seen in the REE pattern of the spring “Oder”, the lake “Oderteich” and the inflow 2 to the reservoir “Oder-Stausee” can be explained by the oxidation of Ce^{3+} and the precipitation of CeO_2 when the spring water gets in contact with oxygen of the air (Elderfield et al., 1990). From the Ce anomaly it can be concluded that water of inflow 1 has a less contact to oxygen than the other sampled waters.

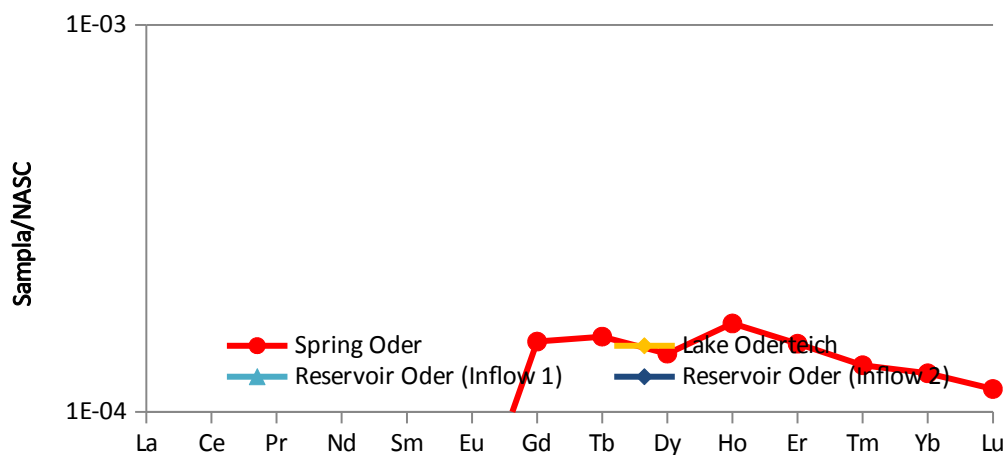


Figure 4: Shale normalised REE pattern of water from the Oder catchment. Spring “Oder” and “lake “Oderteich” show the typical pattern for granitic rocks, whereas the inflows to the reservoir “Oderstausee” have flat pattern typical for greywacke, schist and siltstone.

4.2 Waters connected to greywacke, schist and siltstone of Palaeozoic rock units

The spring of the river “Innerste” (situated in the southeast of Clausthal-Zellerfeld at 605 m a.s.l.) and the spring “Eisenquelle” (situated in the east of Clausthal-Zellerfeld at about 700 m a.s.l.) are connected to carboniferous strata consisting of greywacke, schist and siltstone. Both springs are involved in the water management system “Oberharzer Wasserregal”. The ion concentrations of the springs vary with rain water amount. The typical concentration range of the main ions is shown in Figure 5 for the spring “Eisenquelle”. Due to the atmospheric oxygen supply, brownish iron(III) oxide-hydroxides are precipitating from the spring water. Data from 1974 and 1974 compared to actual data allow the conclusion that only the sulphate concentration is reduced after the air control measures at the end of the last century. All the other ion concentrations are still in the same range. The differences for the K^+ and Na^+ concentrations could be explained by the change of the analytical method (1972-1973: atom absorption spectrometry, 2010-2015: ion chromatography).

REE concentrations are generally lower than in waters from granitic areas. The crust normalised REE pattern of the waters as are flat as the REE pattern of the hosting rocks. But they also reflect the dilution effects due to changes of the rain water amount (Figure 6). The typical Ce anomaly for water with contact to atmospheric oxygen has already been explained in the previous section.

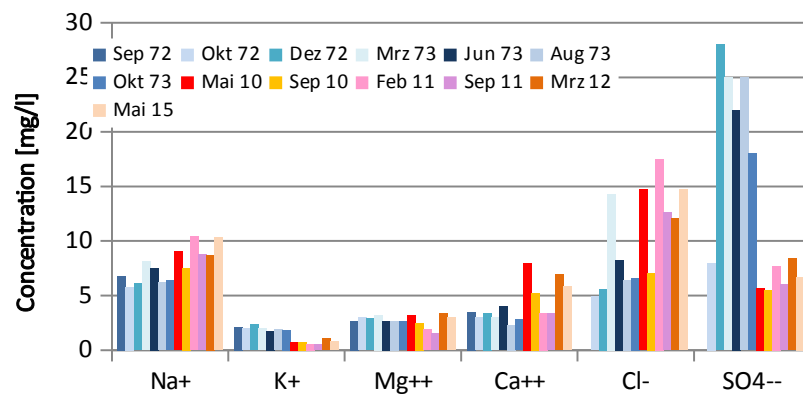


Figure 5: Spring “Eisenquelle” with the precipitation of brownish iron oxide-hydroxides. Main ions of the spring “Eisenquelle” (Data from Alické 1974 and Bozau et al. 2013)

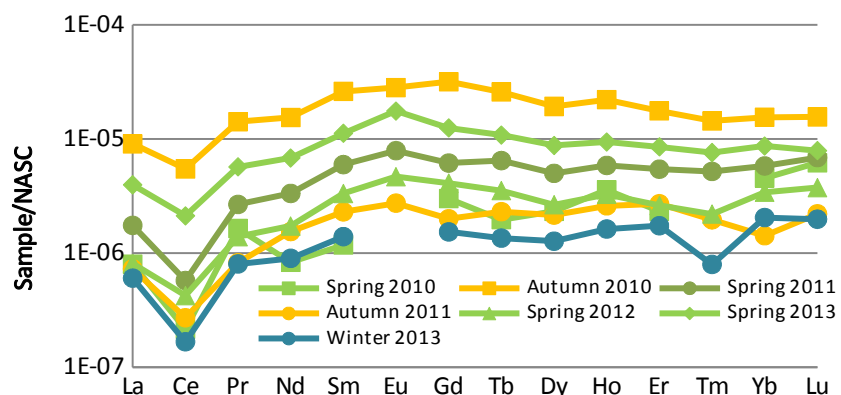


Figure 6: Spring “Innerste”. Temporal variations of the REE pattern of the spring “Innerstequelle” from Mai 2010 to December 2013. Autumn 2010 was very dry and the REE concentrations reach the highest values.

4.3 Rammelsberg mine near Goslar

The Rammelsberg mine, a sedimentary exhalative deposit, is situated in the south of the town Goslar. The orebody with 7 Mt metal content (Mainly Zn, Pb, Cu, Ag and Au were extracted.) was situated in middle Devonian schists consisting of dark shales and tuff bands (Pohl, 1992).

After more than 1000 years the mining activities ended in 1988 due to depletion. The mine is a museum now. Many adits and the dewatering system are still accessible. A water sample was collected in the pumping shaft. The water sample represents a mixture of the water flowing through the mine. The water amount can be correlated to the rain water height. Water chemistry is influenced by the water-ore interaction (Table 1 and 3). High sulphate concentrations (1,100 mg/l) and Zn concentrations (15.3 mg/l) point to the weathering of sulphide minerals. Cu (35 µg/l), Pb (<3 µg/l) and Fe (4 µg/l) concentrations are surprisingly low for an ore mine. Compared to the other water samples B, Li and Sr concentrations are enriched. The formation of secondary minerals, e.g. copper and zinc sulphates (Figure 7), can be seen during a museum tour in the main adits. Interpreting the chemical data it seems to be possible that the dissolution of these secondary

minerals can be responsible for the water composition. REE concentrations in the mine water are low. The REE pattern is comparable to that of the spring waters deriving from greywacke, schist and siltstone as shown for the spring “Innerste” in Figure 7.

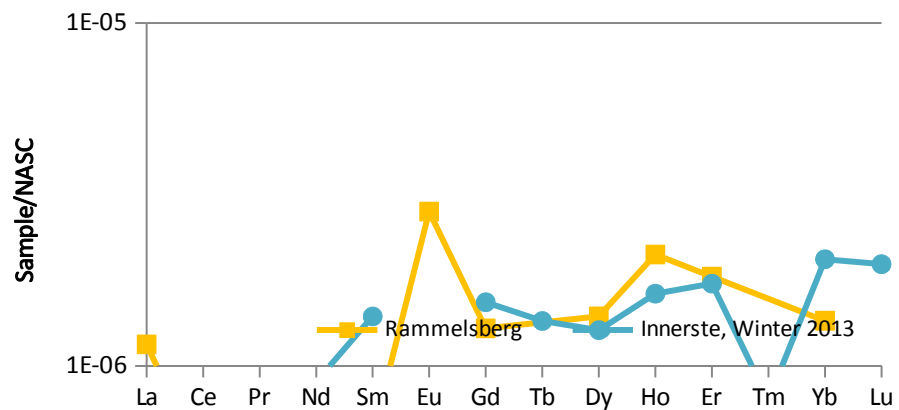


Figure 7: Rammelsberg mine underground (Formation of secondary copper sulphates). REE pattern of the mine water are compared to the spring “Innerste” at a sampling date with high rain water dilution.

4.4 Lake “Blauer See” connected to limestone of the “Elbingeröder Komplex”

The geological unit “Elbingeröder Komplex”, a fossil Devonian reef, is situated east of the Mount Brocken and consists of limestone. Typical karst phenomena including caves developed in that area that belongs to the barrier reef zone of the Variscan Mountain Range. The limestone has been industrially used for a long time. The exploitation started in the 19th century. Today, active open pit mines are found near the town Elbingerode. Furthermore, there are some submarine exhalative iron mineralisations which were mined until the end of the last century. Today some of these pits are show mines, e.g. the pit “Büchenberg” where the formation of calcite precipitation can be observed (Figure 8). The lake “Blauer See” is formed by rain, leakage and ground water which are filling the lowest level of an old open pit limestone mine. Mining in that pit started in 1885 and was abandoned in 1945.

The water has the typical blue colour of lakes in karstic environments which contain many calcite particles. Calcite precipitation indicating a decreasing water table can be seen at the shore of the lake. During summer and autumn, the water colour is changing to green due to algae growth (Figure 8) and the lake sometimes also dries-out.

Water chemistry should be determined by the equilibrium of rain water with calcite and atmospheric CO₂ leading to a pH value of about 8.2. But a pH value of 10 was measured in June 2015 (Table 1) leading to the conclusion that CO₂ is biologically consumed within the lake water so that the mineral calcite alone is buffering the system. In July 2015, the pH increased to 10.6 which could be explained by high evaporation leading to changes in the aqueous complexes (HCO₃⁻ is replaced by CaCO₃⁰) and intense microbiological activities (e.g., photosynthesis, uptake of nitrate, denitrification).

Compared to both, the waters from the granitic area and the area of greywacke, schist and siltstone (Table 3), the lowest trace metal concentrations are found in the water of the lake “Blauer See”. But its water has relatively high concentrations of B, Li and Sr indicating that the Devonian limestone formed from sea water which is enriched in these elements. REE pattern of the water should retain the sea water like REE pattern of the limestone. But because of the low REE concentrations in the limestone, the REE concentrations of the water are below the detection limits of our analytical method.



Figure 8: Limestone of the geological unit “Elbingeröder Komplex”

1) Lake “Blauer See” in June 2015 (pH 10.0)

2) Lake “Blauer See” in July 2015 (pH 10.6)

3) Calcite precipitate on the shore of the lake “Blauer See” after water table decrease in July 2015

4) Dripping stalactite (length about 2 - 5 cm) in the museum mine “Büchenberg”

5. Summary

The investigated waters show that rock-water interaction is an important process leading to different typical water compositions. REE pattern and trace element concentrations can be used as indicators for the interaction of the water with different rocks. Waters connected to granite rocks display higher REE concentrations, an enrichment of heavy REE and the typical negative Eu anomaly, whereas waters from geological units dominated by greywacke, schist and siltstone show lower REE concentrations and mostly flat REE pattern. Mining waters have an increased concentration of Zn, Cu and further trace elements deriving from the ore minerals. Uranium concentrations of mine water and waters from the granitic areas are higher than the uranium concentrations of water connected to limestone and geological units consisting of greywacke, schist and siltstone. Sea water derived elements, e.g. Li and B, are found in mine waters and waters connected to limestone.

The surface water of the Harz Mountains is mainly derived from rain water those ions concentrations are influenced by biological and geochemical processes within the soil and rock as well within the water body itself. The mineralisation of these waters is relatively low compared to water from other regions. These waters are the main basis for a sustainable drinking water production in the dam reservoirs of the Harz Mountains.

Only mine water and deep springs with contact to ore minerals and highly mineralised rock units reach higher concentrations. These waters must be observed and a mixing with the surface water used for drinking water supply must be avoided. But considering the entire territory and the annual volume of low mineralised surface water leaving the Harz Mountains, the influence of the mine water and deep springs is only of local and minor importance.

To sustain the drinking water quality and evaluate the anthropogenic influence the hydrogeochemical data of springs and surface waters in the Harz Mountains should be continuously monitored. As known from industrial sites and highly populated cities, the concentration of micropollutants in waters including trace elements, REE and pharmaceuticals passing waste water plants (e.g., Strauch et al., 2008) are rising worldwide. Japanese rain waters are already enriched in

REE (Iwashita et al., 2011). To minimise an overlapping of natural indicators for rock-water interaction by anthropogenic inputs - even if they are not toxic for the environment - it should be tried to reduce the anthropogenic changes of the water concentrations as much as possible.

Acknowledgements

We thank Mr Willecke from the Rammelsberg mine for organising and assisting the water sampling at the Rammelsberg mine. Mrs Ambrosi and Mr Schmidt (TU Clausthal) are thanked for analysing water samples by IC and ICP-MS.

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