

# Hydrogeochemical characteristics of mine water in the Harz Mountains, Germany

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## ABSTRACT

Water samples (springs, creeks, mine adits) from different former mining districts of the Harz Mountains and the nearby Kupferschiefer (copper shale) basin of Sangerhausen were analysed for major ions and trace metals. Due to more intensive water rock interactions including the ore minerals, the mine water concentrations of main components and trace metals are generally higher compared to non mining affected surface waters of the mountain range. Furthermore, the content of major ions in mine water is enriched by mixing processes with saline waters from Permian layers in the Kupferschiefer district and at the deeper levels of the mines in the Upper Harz Mountains. The waters of the different mining districts can be distinguished by trace metal occurrences and concentrations derived from the different ore bodies. Water from the Kupferschiefer mines shows the highest Na, Cl, Cu, Mo and U concentrations, whereas a combination of elevated As and Se concentrations is typical for most of the samples from the mines around St. Andreasberg. However, there are exceptions, and some water samples of all the investigated mining districts do not follow these general trends. Despite the influence of mining activities and ore mineralisation, hydrochemical effects due to rain water dilution can be seen in most of the waters. According to the elevation of the mountain range, higher precipitation rates decrease the ion concentrations in the waters of springs, creeks and mine adits.

## 1. Introduction

Most German ore mining districts (e.g., Erzgebirge, Harz) have a long history stretching as far back as the Bronze Age (De Vos et al., 2005; Ließmann, 2010; Möller and Lüders, 1993; Monna et al., 2000). The ore deposits were mainly exploited for iron, silver and base metals (Cu, Pb, Zn). Today, the upper levels of many old exhausted mines and their water adits are still accessible. The mine water of the old mines is often closely connected to the meteoric water cycle.

Mining always has an impact on the environment (Hilson and Murck, 2000) and the drainage waters near abandoned mines have to be investigated to outline the behaviour of toxic elements in the environment (Fuge et al., 1993). Water draining abandoned ore and coal mines is often characterised by low pH-values, enriched metal and sulphate concentrations (e.g., Gray, 1997; Cidu et al., 2009) or even by chemicals used for the ore leaching (e.g., Johnson, 2015).

In our study, waters of the different mining districts in the Harz Mountains and the nearby Kupferschiefer (copper shale) basin of Sangerhausen are investigated for major ions and trace metals. The chemistry of these waters is compared with that of present-day

precipitation and surface waters (springs and creeks) of the surrounding areas where water quality should not be influenced by mining. A profound comparison of the measured hydrochemical data from the Harz Mountains with mine water compositions from other regions will be not really practicable because of the special ore types found in the Harz Mountains and the German copper shale basins, the outstanding underground mining system and the relatively high regional precipitation amounts. Furthermore, most published data (e.g., Fuge et al., 1993; Cidu et al., 2014; Desbarats et al., 2016) only refer to single mines with focus on selected trace elements. The aim of our study is the first hydrogeochemical comparison of waters including major ions and trace elements from the different ore mines in the Harz Mountains and the nearby copper shale basins. Furthermore, the results are used for evaluating the impact of mine water in the hydrochemical cycle of the study area.

## 2. Study area and sampling locations

The Harz Mountains in Northern Germany are part of the Rhenohercynian Zone of the Variscan orogenic belt (Fig. 1). The

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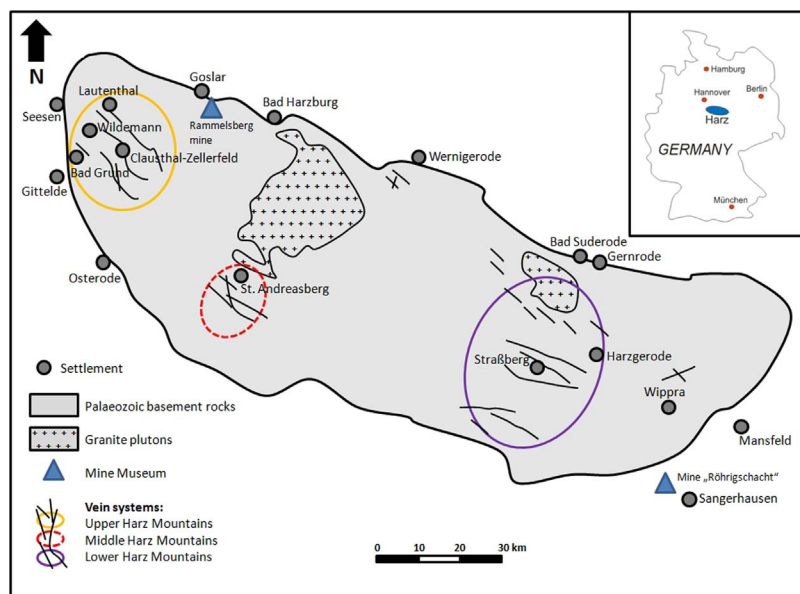


Fig. 1. Sketch of the Harz Mountains highlighting the mining and sampling regions.

mountain area is about 120 km long, about 40 km broad and mainly consists of a fold and thrust sequence of Palaeozoic rocks (Bachmann et al., 2008). The Palaeozoic rocks are intruded by two main Lower Permian postcollisional granite plutons: the Brocken and the Rammberg plutons. The Brocken pluton is dated at about 283 million years (Zech et al., 2010). The Palaeozoic basement is unconformably overlain by Late Permian and Mesozoic sedimentary rocks which were largely eroded during the Tertiary uplift of the Harz Mountains. However, these strata including thick Zechstein and younger evaporite units are still preserved in the surroundings of the Harz Mountains, such as the Sangerhausen basin.

The Harz Mountains are known for their important metal deposits including the world-class Rammelsberg massive sulphide deposit (syngenetic Devonian SEDEX mineralisation) as well as numerous post-orogenic polymetallic veins (Large and Walcher, 1999; Pohl, 1992). The ore veins of the Upper and Middle Harz Mountains have traditionally been considered to be related to the granitic intrusions. But since the 1990s, the hydrothermal vein mineralisations are thought to have developed during repeated post and anorogenic rifting from the Late Carboniferous to the Late Cretaceous (Lüders and Möller, 1992).

There is a regional metal zonation. While Ag-rich Pb (galena, tetrahedrite) and Zn (sphalerite) in quartz carbonate gangue around Clausthal-Zellerfeld and Bad Grund are found, the St. Andreasberg district with a similar main mineralogy has in addition a broad variety of arsenic and antimony minerals. The hydrothermal vein systems in the eastern part of the Harz Mountains, such as the large vein system of Strassberg-Neudorf, which reaches 15 km strike length, mainly carry fluorite, quartz and calcite combined with minor ore minerals such as chalcopyrite, arsenopyrite, galena, sphalerite, wolframite, scheelite and siderite (Dahlgrün, 1950; Wilke, 1952; Stedingk and Stoppel, 1993; Schneider et al., 2003; Ließmann, 2010). Observations of brines in the deeper levels of the mines in the Upper Harz Mountains are reported by Carlé (1975) and Lattermann and Müller (1889) who described a brine discharging with 40 L/s at the 13th level of the ore mine “Lautenthalsglück”. Mohr (1993) explained the occurrence of these waters by a migration of saline waters from the Permian rock units at the western margin of the mountain range along the about 7 km long fault zones connected to the mined ore veins (see supplementary information).

The basins of Sangerhausen and Mansfeld at the southeast boundary of the Harz Mountains are known for their stratiform copper mineralisation in the Permian Kupferschiefer (Wagenbreth and Steiner, 1990). This type of hydrothermal mineralisation has a broad spectrum

of redox-sensitive and chalcophile metals, including Pb, Zn, Ag, V, Se, Au, Mo, Ni, Re, Ge, Cd, U, As, Sb, Bi, Se, Tl and platinum group elements (Vaughan et al., 1989).

The precipitation rate in the Harz Mountains increases with altitude. Average yearly precipitation amounts as reported by Tonn (2002) are for Clausthal, Mount Brocken and the area around Strassberg 1300 mm, 1800 mm and 596 mm, respectively.

Hydrogeochemical studies of the Harz Mountains dealing with surface waters have been performed for many years and identified a variety of anthropogenic-sourced processes (e.g., Aliche, 1974; Andree, 1993; Matschullat et al., 1994; Roostai, 1997; Bozau et al., 2015b). Due to the complex geological situation of the Harz Mountains, the long mining history and many other anthropogenic influences (e.g., atmospheric deposition), the hydrogeochemical composition of the waters results from different and complex geneses. The high trace metal concentrations of mining dumps and soils derived by atmospheric transport from ore dressing plants in some valleys of the Western Harz Mountains (Matschullat et al., 1994) do not prohibit the drinking water supply in this area. Data of Gäbler and Schneider (2000) indicate trace element enrichments in creek sediments and surface soils due to mining and ore conditioning activities, especially in the Upper Harz Mountains. These high enrichments are only locally seen in some surface water samples. Mainly the particulate fraction of the water displays the higher contents whereas the soluble fraction is often not affected (Bozau et al., 2015b). Schneider et al. (2016) define geogenic background concentrations for the total and dissolved fractions of the creek and river waters within the Harz Mountains.

### 3. Methods – sampling and chemical analyses

Mine water samples were taken in the former mining districts of Clausthal, St. Andreasberg, Strassberg-Neudorf and Sangerhausen. Depending on the accessibility, the water was sampled within the mine or at the surface, at the portal of the adits. Additionally, mine ponds near Clausthal-Zellerfeld and one creek (Oder) draining the peat bogs around Mount Brocken were sampled to determine the background values of areas not affected by mining. A detailed description of the sampling points is given in Table 1. The sampling locations are shown in Fig. 1. Four further figures and detailed information of the investigated mining districts are given in the supplementary material. Field parameters (pH, temperature and specific electrical conductivity) were measured directly at the sampling points. The water was filtered through a 0.45 µm Millipore membrane filter for ion chromatography

**Table 1**

Sampling points in the different mining districts of the Harz Mountains (Previously published data of waters from the Rammelsberg mine and the Mansfeld basin are added.) The elevation of the adits is given in meter above sea level (a.s.l.).

Mining district	Sampling point	Sampling number Fig. 7	pH	SEC [ $\mu\text{S}/\text{cm}$ ]
<b>Upper Harz Mountains</b>				
<b>Mines around Clausthal</b>				
Mine "Lautenthalsglück"	Adit "Ernst-August-Stollen" (Inflow of deeper levels)	10	7.8	1020
	Adit "Ernst-August-Stollen" ("Hafen")	11	7.5	946
Adit portal	Adit "Ernst-August-Stollen" (Gittelde), 189 m a.s.l.	14	8.2	1173
	Adit "Tiefer Georg" (Bad Grund), 286 m a.s.l.	13	9.8	448
	Adit "13-Lachter-Stollen" (Wildemann), 383 m a.s.l.	12	7.9	345
Mine ponds/reservoirs	Carler Teich (Fig. 4 – 18)		8.2	267
	Unterer Stadtweger Teich (Fig. 4 – 16)		7.4	237
	Oberer Stadtweger Teich (Fig. 4 – 14)		7.6	158
	Unterer Eschenbacher Teich (Fig. 4 – 11)		8.0	123
	Oberer Eschenbacher Teich (Fig. 4 – 7)		7.6	84
	Oberer Hausherzberger Teich (Fig. 4 – 4)		7.5	75
<b>Rammelsberg Mine</b>				
Drainage Adit <sup>a</sup>			6.5	1870
<b>Middle Harz Mountains</b>				
<b>Mines in St. Andreasberg</b>				
Mine "Samson"	Adit "Grünhirschler Stollen", 457 m a.s.l.	1	7.6	390
	Adit "Sieberstollen", 390 m a.s.l.	2	7.9	327
	Adit "Sieberstollen", 390 m a.s.l.	3	7.5	302
Mine "Gnade Gottes"	Adit "Grünhirschler Stollen", 457 m a.s.l.	8	7.2	264
Mine "Wennsglückt"	Adit "Tagesstollen-Feldort"	7	7.5	118
	Stagnant Pool "Tagesstollen"	9	7.1	134
	Adit "Tagesstollen", North inflow	4	7.6	365
Mine "Roter Bär"	Adit "Tagesstollen", East inflow	5	7.7	223
	Adit "St. Annenstollen", 590 m a.s.l.	6	8.1	179
Adit portal				
<b>Lower Harz Mountains Vein system "Strassberg-Neudorf"</b>				
	Drainage adit of the 2nd level in Mine "Glasebach"	15	8.1	727
<b>Kupferschiefer</b>				
<b>Sangerhausen Basin</b>				
Mine "Röhrigschacht" (Wettelrode)	Adit "Segen-Gottes-Stollen"	18	7.8	45,000
	Inflow A	16	7.9	22,200
	Inflow B	17	7.6	60,000
<b>Mansfeld Basin</b>				
Adit portal <sup>b</sup>	Adit "Schlüsselstollen"		7.4	45,000
<b>Oderbrück</b>				
Creek "Oder"	Background value for surface water on the granitic basement of the Upper Harz		6.2	50

<sup>a</sup> Data from Bozau et al. (2015c).

<sup>b</sup> Data from Baborowski and Bozau (2006).

and ICP-MS analyses. The sample aliquot for ICP-MS measurements was acidified with concentrated  $\text{HNO}_3$  directly after sampling and filtration. The measured elemental concentrations of the filtrated water samples (filter pore size  $0.45 \mu\text{m}$ ) consist of the "true" dissolved aqueous species, colloids and nanoparticles.

The water samples were analysed for major ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$ ) by ion chromatography (DIONEX, Germany) with a standard error of  $\pm 5\%$  at the University of Göttingen (Department of Applied Geosciences). Further element measurements were carried out with an ICP-MS (inductively coupled plasma mass spectrometry) at Bureau Veritas (formerly ACME), Vancouver, Canada. The analytical data with a standard error of  $\pm 10\%$  and the detection limits are given in Table 2. Three water samples with high salt concentrations (Kupferschiefer district, mine "Röhrigschacht") had to be diluted for the ICP-MS analysis. Therefore, the detection limits of these three water samples are 100 times higher than for the non diluted samples.

The concentration of hydrogen carbonate of the mine water was estimated by the missing negative charge within the ion balance calculation of each sample because a titration with  $0.1 \text{ M HCl}$  was not possible at most of the sampling locations, and the sample volume had

to be reduced due to partly difficult access for underground locations. Thermodynamic calculations to determine saturation indexes and ion balances were performed using the code PHREEQC and the database "phreeqc.dat" (Parkhurst and Appelo, 1999).

#### 4. Results and discussion

First the field parameter and chemical data of all investigated mine waters will be discussed and their relations to other elements of the water cycle in the Harz Mountains (Fig. 2) will be shown. At the end of this section the trace element data for each mining district are compared and evaluated.

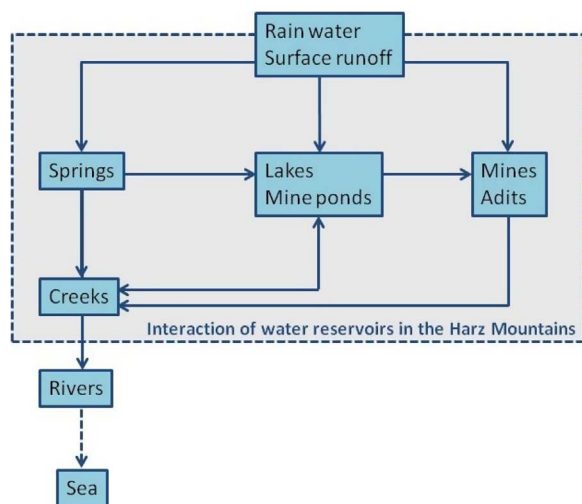
##### 4.1. pH value and specific electrical conductivity

The measured pH values of the mine water range between 6.2 and 8.2 (Table 1). The pH values lower than 7 can be explained by an increased input of rain water and minor effects of water rock interaction. Rain water measured at Clausthal-Zellerfeld displays pH values from 4.4 to 6.8 (Bozau et al., 2015a), and water in equilibrium with calcite should reach a pH value of about 8.2.

**Table 2**  
Average (minimal–maximal) concentrations of the mine water samples (n = number of samples).

	D.L.	Mining district St. Andreasberg n = 9	Mining district Clausthal n = 5	Mining district Kupferschiefer <sup>a</sup> Dilution1:100 n = 3	Glasebach n = 1	Creek Oder n = 1	Mine ponds Clausthal n = 6
mg/L							
Ca	0.05	29 (12–45)	106 (33–191)	1340 (1150–1600)	102	2	12 (5–24)
Mg	0.05	6 (3–11)	24 (12–37)	128 (115–146)	26	0.6	3 (2–5)
Na	0.05	9 (3–17)	36 (14–98)	9050 (4100–13400)	14	3	10 (2–19)
K	0.05	1.3 (0.5–2.9)	4.6 (2.1–8.2)	23 (18–27)	7	0.9	1.7 (0.5–6.3)
Cl	1	26 (1–45)	24 (17–35)	12700 (6000 – 18800)	22	1	15 (2–34)
SO <sub>4</sub>	3	18 (9–33)	219 (42–387)	2610 (2400–3000)	186	6	18 (12–30)
SiO <sub>2</sub>	0.1	12 (10–15)	8 (7–10)	< 10 (< 10–23)	13	11	0.4 (< 0.1–1.1)
µg/L							
Ba	0.05	9 (0.3–57)	54 (22–108)	37 (19–49)	16	14	31 (22–57)
Sr	0.01	96 (37–267)	478 (84–789)	10400 (7930–13340)	362	12	53 (19–99)
Cs	0.01	0.2 (0.1–0.7)	0.9 (0.4–2.1)	24 (12–48)	0.7	0.03	0.07 (0.02–0.19)
Li	0.1	10 (4–20)	26 (4–37)	90 (70–110)	33	1	0.4 (0.3–0.7)
Br	5	18 (11–28)	27 (21–45)	2430 (1100–3500)	42	12	18 (13–23)
Al	1	4 (2–7)	3 (< 1–7)	670 (500–800)	456	173	15 (1–27)
Fe	10	< 10 (< 10–65)	2015 (< 10–2300)	< 1000	3220	367	60 (24–94)
Mn	0.05	49 (0.3–282)	538 (2–1330)	560 (460–640)	6150	39	13 (3–22)
Cu	0.1	1.3 (0.2–3.8)	2.1 (1.5–2.9)	180 (80–360)	96	0.7	1.0 (0.6–1.4)
Cd	0.05	0.3 (< 0.05–0.6)	0.3 (0.1–0.4)	< 5	0.2	0.2	0.09 (0.06–0.2)
Pb	0.1	4 (< 0.1–20)	2.8 (< 0.1–4.8)	70 (60–80)	0.1	8	1.8 (0.4–4.2)
Zn	0.5	50 (3–192)	1190 (23–3120)	713 (410–1050)	46	11	13 (3–32)
Ni	0.2	1.3 (< 0.2–2.6)	34 (< 0.2–73)	30 (< 30–30)	22	0.3	0.5 (0.3–0.9)
Co	0.02	0.1 (< 0.02–0.3)	12 (< 0.02–28)	4 (2–7)	0.08	0.2	0.06 (0.02–0.1)
Cr	0.5	1.2 (< 0.5–1.5)	< 0.5 (< 0.5–2.8)	< 50	3	0.2	< 0.5 (< 0.5–0.5)
Mo	0.1	0.5 (0.2–0.7)	0.8 (< 0.1–1.9)	53 (30–70)	0.3	< 0.1	< 0.1
W	0.02	< 0.02 (< 0.02–0.03)	< 0.02 (< 0.02–0.02)	< 2	0.03	0.03	< 0.02
Sn	0.05	< 0.05	< 0.05	< 5 (< 5–5)	< 0.05	0.06	< 0.05
As	0.5	(3–199)	22 (< 0.5–37)	75 (< 50–90)	5	0.8	< 0.5
Sb	0.05	10 (0.2–70)	0.9 (0.8–1.0)	8 (< 5–10)	0.1	0.2	0.7 (0.3–1.2)
Se	0.5	1.0 (0.6–1.2)	< 0.5 (< 0.5–0.7)	< 50	< 0.5	< 0.5	< 0.5
Ge	0.05	< 0.05	0.08 (< 0.05–0.08)	< 5	< 0.05	< 0.05	< 0.05
La	0.01	0.03 (< 0.1–0.06)	< 0.01 (< 0.01–0.03)	3 (1–6)	2	0.9	0.02 (0.01–0.05)
Ce	0.01	0.01 (< 0.01–0.03)	< 0.01 (< 0.01–0.07)	< 1	4	0.8	0.03 (0.01–0.1)
Pr	0.01	< 0.01 (< 0.01–0.01)	< 0.01	< 1	0.5	0.2	< 0.01 (< 0.01–0.01)
Nd	0.01	< 0.01 (< 0.01–0.07)	0.03 (< 0.01–0.04)	< 1	2.3	0.8	< 0.01 (< 0.01–0.07)
Sm	0.02	< 0.02	< 0.02	< 2	0.5	0.2	< 0.02
Eu	0.01	< 0.01	< 0.01	< 1	0.3	0.02	< 0.01
Gd	0.01	< 0.01 (< 0.01–0.02)	0.03 (< 0.01–0.04)	< 1 (< 1–1)	0.6	0.3	0.02 (0.01–0.02)
U	0.02	0.3 (< 0.02–1.0)	0.5 (0.2–0.8)	15 (12–19)	0.2	0.09	< 0.02
Th	0.05	< 0.05	< 0.05	< 5	< 0.05	< 0.05	< 0.05

<sup>a</sup> Due to dilution for chemical analyses the detection limits (D.L.) of the samples from the mine “Röhrigschacht” (Sangerhausen Basin) are enriched by 100.



**Fig. 2.** Elements of the regional water cycle in the Harz Mountains.

The specific electrical conductivities (SEC) of the investigated mine waters allow for some general remarks on the water quality in the Harz Mountains (Fig. 3). The mine waters originate from meteoric water (rain and surface runoff) and the water conducted to the mines from the

mine ponds which, in turn, are fed by rain, surface runoff, springs and creeks. Conductivities in the rain water of Clausthal-Zellerfeld range between 5 and 43 µS/cm. The spring water is enriched in ions due to soil and rock water interactions. According to the elevation of the mountain range combined with higher precipitation rates the SEC of the springs on granitic rocks around Mount Brocken is lower than the SEC of the springs on greywacke around Clausthal-Zellerfeld. Seasonally, the SEC of the springs is changing: high precipitation rates lead to an increased dilution of the spring waters (Bozau et al., 2013). The SEC of the mine ponds varies between 30 and 250 µS/cm. Some mine ponds nearly display rain water values, but most of the ponds are fed by spring water, which results in higher solute content. Furthermore, anthropogenic influences and intensive lake internal processes contribute to an increasing SEC (Bozau et al., 2015b). Compared to the spring water samples, the ponds display a nearly constant SEC in all seasons and do not closely respond to changing precipitation rates (Fig. 4a and b).

The mine water samples of the districts around Clausthal and St. Andreasberg show the same elevation effect as the spring waters connected to greywacke (e.g., Innerste spring) and granite, respectively (Fig. 3). Therefore, mine water in St. Andreasberg is more diluted by meteoric water compared to the waters from the mines around Clausthal where the precipitation rate is lower. But due to the intensified water rock interactions within the adits, the SEC values of the mine waters are generally higher than in the springs. Furthermore, the inflow

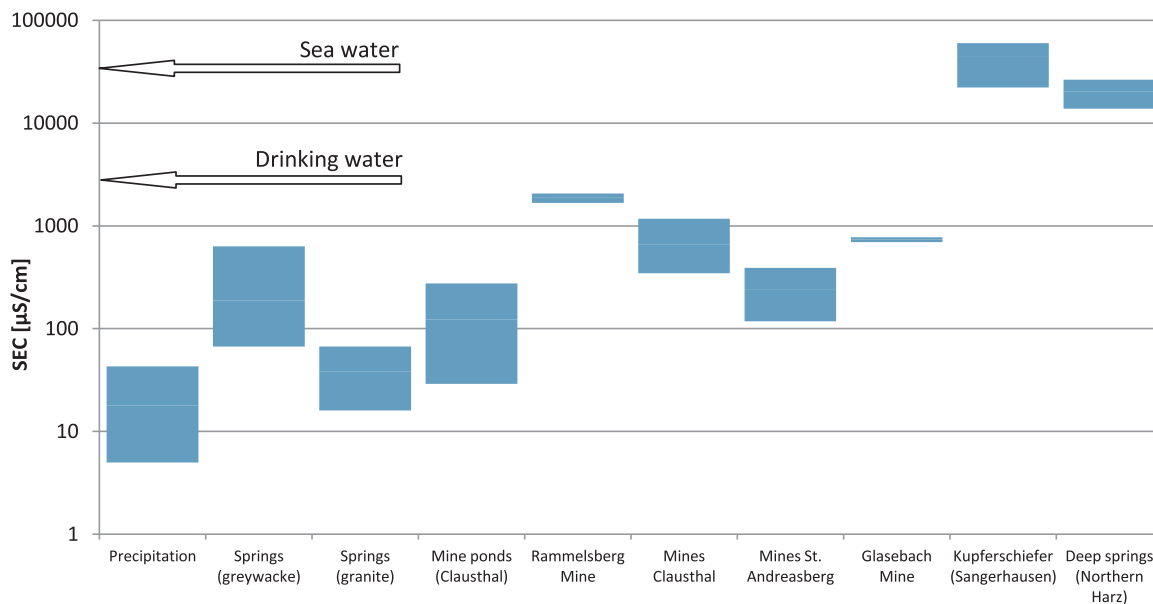


Fig. 3. Specific electrical conductivities (SEC) of waters in the Harz Mountains (after Bozau et al., 2015a,b,c) including the SEC of sea water and the maximal level of SEC allowed for German drinking water.

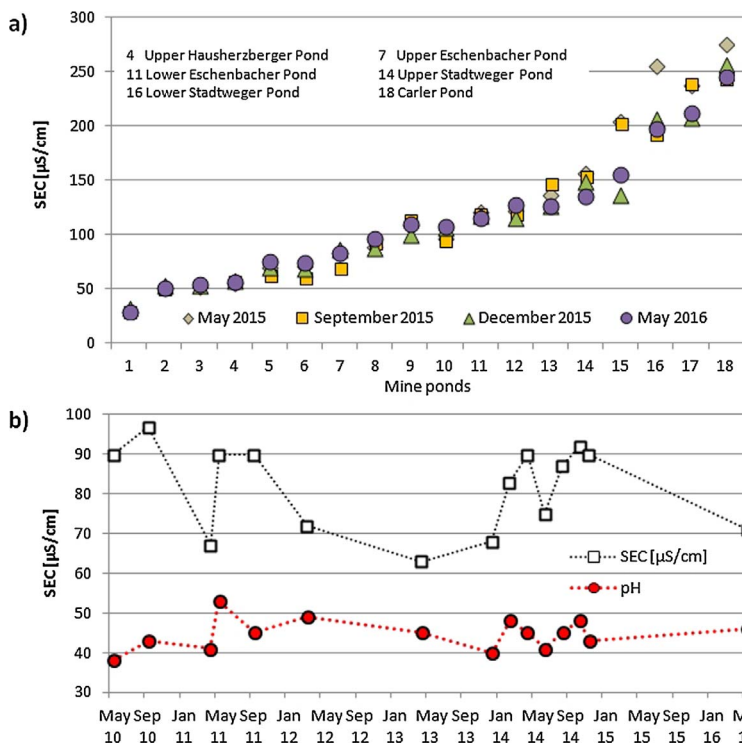


Fig. 4. Temporal variations of the specific electrical conductivities (SEC) of surface waters in the Upper Harz Mountains around Clausthal-Zellerfeld. a) Mine ponds arranged according to rising SEC (The names of the six ponds investigated in detail are given in the legend.) b) Spring of the Innerste river

of deep brines to the upper levels of the mine “Lautenthalsglück” leads to increasing SEC values of the waters sampled in the adit “Ernst-August-Stollen” within the mine (Table 1: sample 10 and 11) and at the adit portal (Table 1: sample 14).

The Glasebach mine in the eastern part of the Harz Mountains with lower precipitation amounts shows SEC comparable to the samples of the mining district around Clausthal. The samples from the Kupferschiefer mine “Röhrigschacht” reach SEC values comparable to sea water and exceed the SEC values of the deep springs in Bad Harzburg and Bad Suderode at the northern boundary of the Harz Mountains (Bozau and van Berk, 2014). These high SEC values result from halite dissolution in the overlying Permian salt layers by meteoric water flowing to the Kupferschiefer mines afterwards.

4.2. Sodium, calcium, magnesium, chloride and sulphate

Natural sources of sodium and chloride in terrestrial environments include contributions from atmospheric deposition, soil water and rock water interactions and the inflow of basinal brines (Kelly et al., 2010; Nordstrom et al., 1989; Panno et al., 2006). Fig. 5 shows the molal Na and Cl concentrations measured in the mine water samples of the Harz Mountains. Data for rain and spring water sampled around the town of Clausthal-Zellerfeld from 2010 to 2014 are added (Bozau et al., 2015a). The Na and Cl concentrations of rain water are derived from sea water spray and show the lowest values. The Na/Cl ratio equal to 1 measured in the water samples is usually attributed to halite dissolution (halite solubility line). In Fig. 5 the rain water and the waters of the

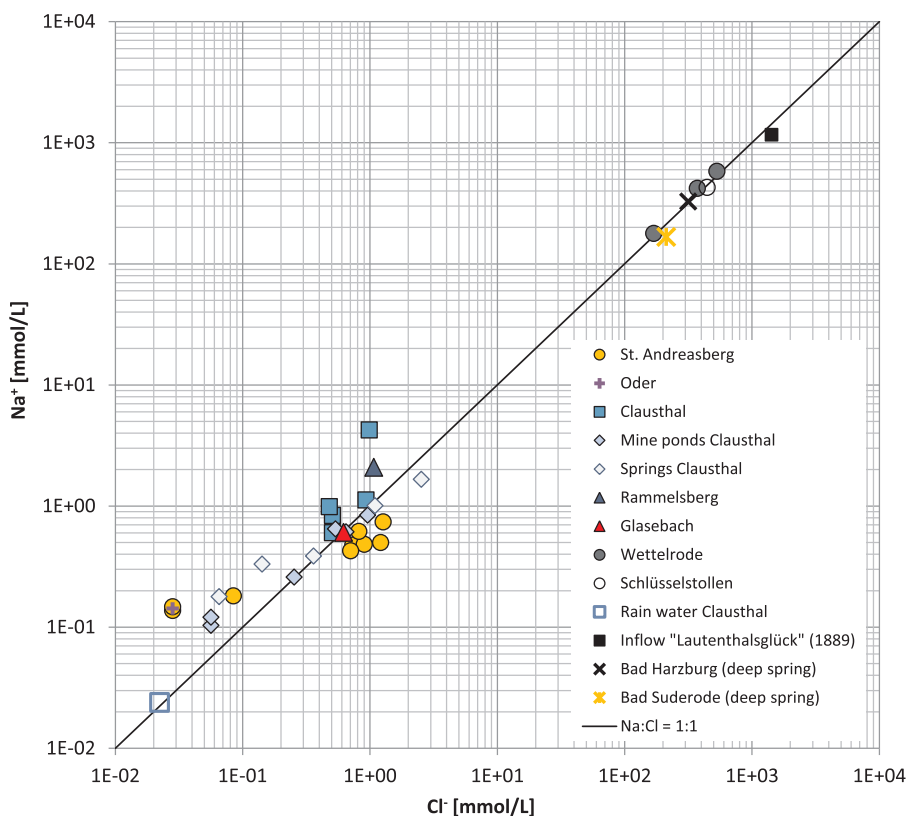


Fig. 5. Relation between sodium and chloride in water samples from the Harz Mountains.

Kupferschiefer mines mark the start and end point of the halite solubility processes in the study area. The chemical data of the inflow from deeper levels to the adit “Ernst-August-Stollen” in the mine “Lautenthalsglück” from 1889 (in [Carlé, 1975](#)) display a slight Na decrease which is compensated by Ca. As known for deep springs in Bad Harzburg and Bad Suderode at the northern boundary of the Harz Mountains ([Bozau and van Berk, 2014](#)), rising Ca concentrations are related to hydrogeochemical processes in deeper layers (Lower Buntsandstein and Permian strata) and Na/Cl ratios equal to 1 are characteristic for waters deriving from halite dissolution of upper strata (e.g. Muschelkalk). Furthermore, molal Cl/Br ratios of the waters from the Kupferschiefer district are higher than 3000 also indicating the dissolution of halite (e.g., [Walter et al., 1990](#)). These Cl/Br ratios also exclude mixing processes with connate sea water. Summarising all the known chemical data and geological facts, the genesis of the waters in the Kupferschiefer mining district and the deeper levels of the mines around Clausthal must be different, although TDS contents are within the same range. Many other water samples, e.g. Glasebach mine, springs connected to upper horizons and most of the ponds dominated by rain water supply and slightly influenced by soil water interaction processes, display the Na/Cl ratio about 1 attributed to halite dissolution.

The waters of the adit “Ernst-August-Stollen”, the Rammelsberg mine, and the creek “Oder” of the granite area show a Na excess. Such an excess can be explained by rock water interactions. Sodium can be released by silicate weathering and ion exchange processes. When calcite and gypsum are dissolved calcium, hydrogen carbonate and sulphate concentrations are rising. Additionally, the divalent Ca is preferentially sorbed onto clay minerals whereas Na is released from the ion exchange sites (e.g., [Fisher and Mullican, 1997](#)) modifying the Na/Cl ratio.

Mine waters displaying a Cl excess are observed in the deeper parts of the mines in St. Andreasberg and a spring of the Clausthal area (“Schwefelquelle”). Starting with the rain water Na/Cl ratio equal to 1, the Cl excess could be explained by decreasing Na concentrations. The missing Na amount ( $Cl - Na$ ) of the samples is also not compensated by

a single cation. Other cations (e.g., calcium, magnesium, potassium) replace the missing Na. Due to the dissolution of calcite, gypsum, silicate and other minerals, the concentration of calcium is higher than the sodium concentration. The potassium concentration is lower than the sodium concentration, and the concentration of magnesium is lower than sodium and higher than the potassium concentration which is typical for terrestrial surface waters. According to the close contact of the investigated waters showing a chloride excess to the meteoric water cycle, an influence of deep brines by mixing processes is also not suitable to explain the chloride enrichment. Furthermore, the chloride excess known from the deeper levels of the mine “Lautenthalsglück” (measured in 1889) is not high enough to explain the chloride enrichment. The Na/Cl ratio of the inflow to the mine “Lautenthalsglück” is 0.82, whereas the average Na/Cl ratio of the other samples below the halite dissolution line is 0.66. Albitisation is a well-known process for Ca enrichment combined with Na reduction in deeper groundwaters. But there are no observations of such a feldspar transformation at the ore veins of the mines. Historical observations of the mineral chlorargyrite (AgCl) combined with clay minerals (so called “Buttermilcherz”) are known from the weathering zones of the old mines in St. Andreasberg ([Hoppe and Damaschun, 1986](#)). Maybe geochemical transformation processes of chlorargyrite and the precipitation of silver sulphide or solid silver in deeper parts of the mines could result in a release of chloride.

Despite chloride, hydrogen carbonate and sulphate are the main anions of the investigated waters. Due to the sampling conditions in the underground mines, the hydrogen carbonate concentrations were not determined by titration. But the values are estimated by the missing anions of the ion balance calculations using the code PHREEQC. Ca and  $HCO_3$  are quite well correlated in the samples of the mine ponds (data in [Bozau et al., 2015b](#)). The hydrogen carbonate concentrations exceed the chloride and sulphate concentrations of samples with chloride concentrations lower than 10 mg/L. The calcium and magnesium vs. sulphate plots of the investigated samples are shown in [Fig. 6](#). The calcium, magnesium and sulphate concentrations rise with increasing

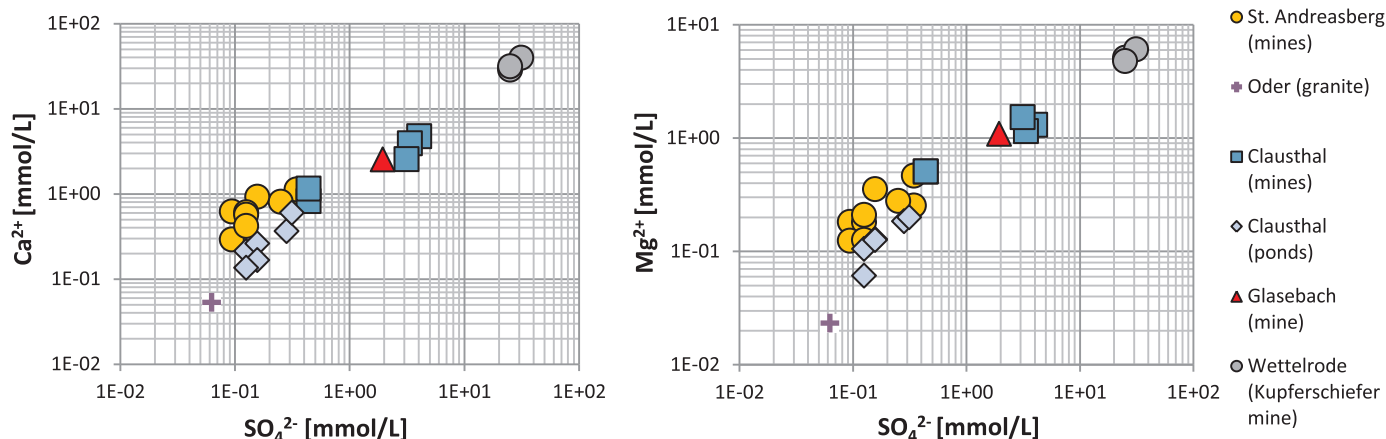


Fig. 6. Relation between calcium, magnesium and sulphate in water samples from the Harz Mountains.

SEC values. The samples from the mining district around Clausthal are characterised by higher calcium, magnesium and sulphate concentrations than the samples from the mines around St. Andreasberg. The lowest concentrations are found in the creek “Oder”. The samples from the mining district “St. Andreasberg” seem to be enriched in sulphate compared to the sulphate concentrations of the mine ponds around Clausthal. However, the difference within the sample group of “St. Andreasberg” seen in Na/Cl ratios is not evident for Ca/SO<sub>4</sub> and Mg/SO<sub>4</sub> ratios.

Due to the different local geological situation, there are also differences in the water samples collected in the mines around Clausthal. The water sampled at three different points of the adit “Ernst-August-Stollen” displays higher concentrations of the major ions than the water from the adit “13-Lachter-Stollen” and the adit “Tiefer Georg”. The rocks drained by the adit “Ernst-August-Stollen” leaving the Harz Mountains contain Permian strata with carbonate layers whereas the other adits are mainly connected to Carboniferous greywackes and shales.

#### 4.3. Silica and fluoride

High SiO<sub>2</sub> concentrations in water samples can be explained by silicate weathering processes (Matthess and Pekdeger, 1980). The water of the district “St. Andreasberg” and the water of the mine “Glasebach” display higher SiO<sub>2</sub> concentrations indicating more intensive weathering processes and different silicate mineral assemblages than the samples of the mines around Clausthal (Table 2). The highest SiO<sub>2</sub> concentration was measured in the drainage adit “Segen-Gottes-Stollen” of the mine “Röhrigschacht” whereas the other two samples of this mine display lower values. The lowest SiO<sub>2</sub> concentrations are found in the mine ponds. These values can be explained by relatively high amounts of rain water and relatively low water rock interactions compared to the mine waters. Furthermore, lake internal biological processes (uptake of silica by diatoms) also can lower the SiO<sub>2</sub> concentrations.

Fluoride concentrations higher than the detection limit of 0.5 mg/L were measured only in the sample of the mine “Glasebach” (mining district “Strassberg-Neudorf”) where fluorite (CaF<sub>2</sub>) is the main vein mineral. The measured value of 3.2 mg F<sup>-</sup>/L exceeds the WHO guideline (2011) of 1.5 mg F<sup>-</sup>/L for drinking water. Data of nine water samples from 2000 (Wolkersdorfer and Hasche, 2001) display an average fluoride concentration of 7 mg/L in the drainage water of the mine “Glasebach”. The fluoride concentration of the creek “Oder” measured in 2016 is about 0.5 mg/L and reflects the interaction of creek water with the surrounding granite which contains more fluoride than the Palaeozoic greywackes and shales in the other mining districts. Igneous and metamorphic rocks contain fluoride within minerals such

as amphiboles and micas, where the hydroxyl position is substituted by fluoride (Edmunds and Smedley, 2005). During weathering processes fluoride is released from these minerals. The fluoride concentration of the water from the mine “Glasebach” should be limited by the fluorite solubility of the vein mineral which was proven by a thermodynamic calculation with the code PHREEQC. Using the measured water composition the calculated saturation index for fluorite was 0.05 indicating equilibrium conditions. The major aqueous fluorine species is fluoride.

#### 4.4. Trace elements

The geochemical signatures of the ore mineralisation in the different mining districts should be reflected in the waters draining the old adits and mines. In particular, the measured trace metal concentrations should be useful to distinguish the waters in contact with the different ore bodies. As expected from the geological situation and mineralisation style as well as the chloride concentrations facilitating salting-in effects, water from the Kupferschiefer mines shows the highest Cu, Mo and U concentrations, whereas a combination of enriched As, Sb and Se concentrations is typical of most of the samples from the mines around St. Andreasberg. But as clearly seen in Fig. 7 and Table 2, some water samples of all the investigated mining districts do not follow these general trends. Furthermore, the same adits sampled at different points show distinctive chemical variations. The water at the portal of the adit “Ernst-August-Stollen” is enriched in Na, Cl, Li, B, Br and other elements typical for salt dissolution whereas the water in the mine “Lautenthalsglück” displays higher Ca, Fe, Mn, As, Ni, Co, Pb and Zn concentrations. No differences are seen for U. The differences of Na and Ca are already explained by different genesis/contact to different rock units in the previous section.

Large differences are found for As and Sb in the adit “Sieberstollen” (St. Andreasberg district). The water sampled in the mine “Fünf Bücher Moses” has a concentration of 199 µg As/L and 70 µg Sb/L, whereas 19 µg As/L and 7 µg Sb/L are measured in the mine “Gnade Gottes”. The high As and Sb concentrations in the mine “Fünf Bücher Moses” can be explained by the local occurrence of rare minerals like gersdorffite, a nickel arsenic sulphide and annabergerite, a hydrous nickel arsenate mineral (Ließmann, 2010).

Because the chemical measurements were done without pre-concentration, some important ore elements could not be determined due to the low solubility of their ore minerals and the analytical detection limits: e.g., selenium concentrations higher than the detection limit were only found in 4 of 9 samples from the mining district “St. Andreasberg” and in 1 of 5 samples from the mining district “Clausthal”. Silver concentrations are lower than 0.05 µg/L in all sampled waters and the concentrations of middle and heavy rare earth elements also do not exceed the analytical detection limits so that rare

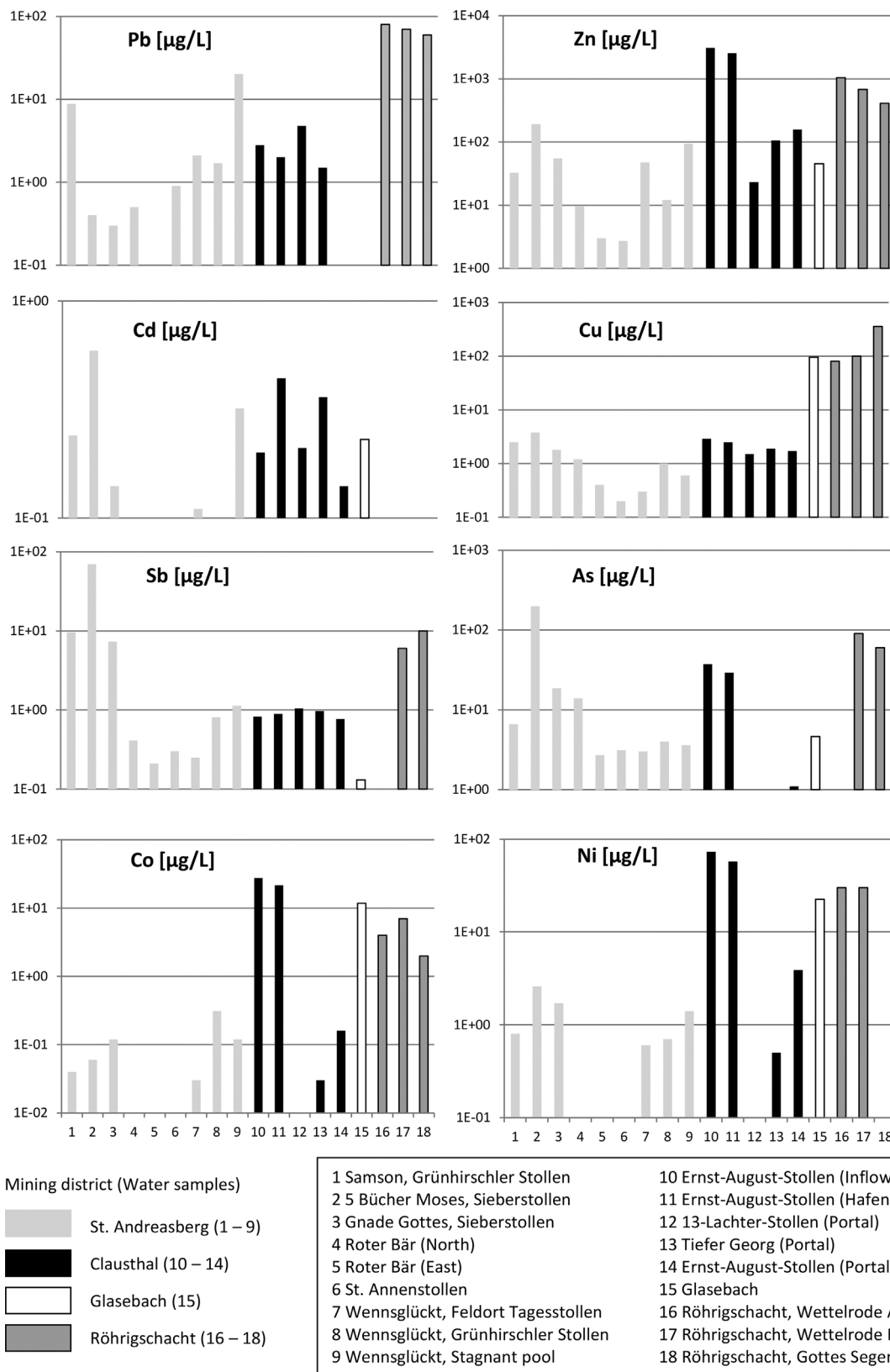


Fig. 7. Trace metal concentrations of the mine waters.

earth element (REE) pattern could not be studied here.

Because of the limited number of samples, correlation coefficients and average concentrations are not really helpful to simplify the classification of the water samples. For example, Co and Ni are well correlated for all samples ( $R = 0.96$ ). But  $R$  for the mine water of St.

Andreasberg is  $-0.22$ , whereas  $R$  equal to 1 is found for the samples around Clausthal. There is a good correlation between Zn and Sb in the mining district “St. Andreasberg” ( $R = 0.88$ ), but no relation between Zn and Sb is seen in the mine water collected in the mines around Clausthal ( $R = -0.41$ ).



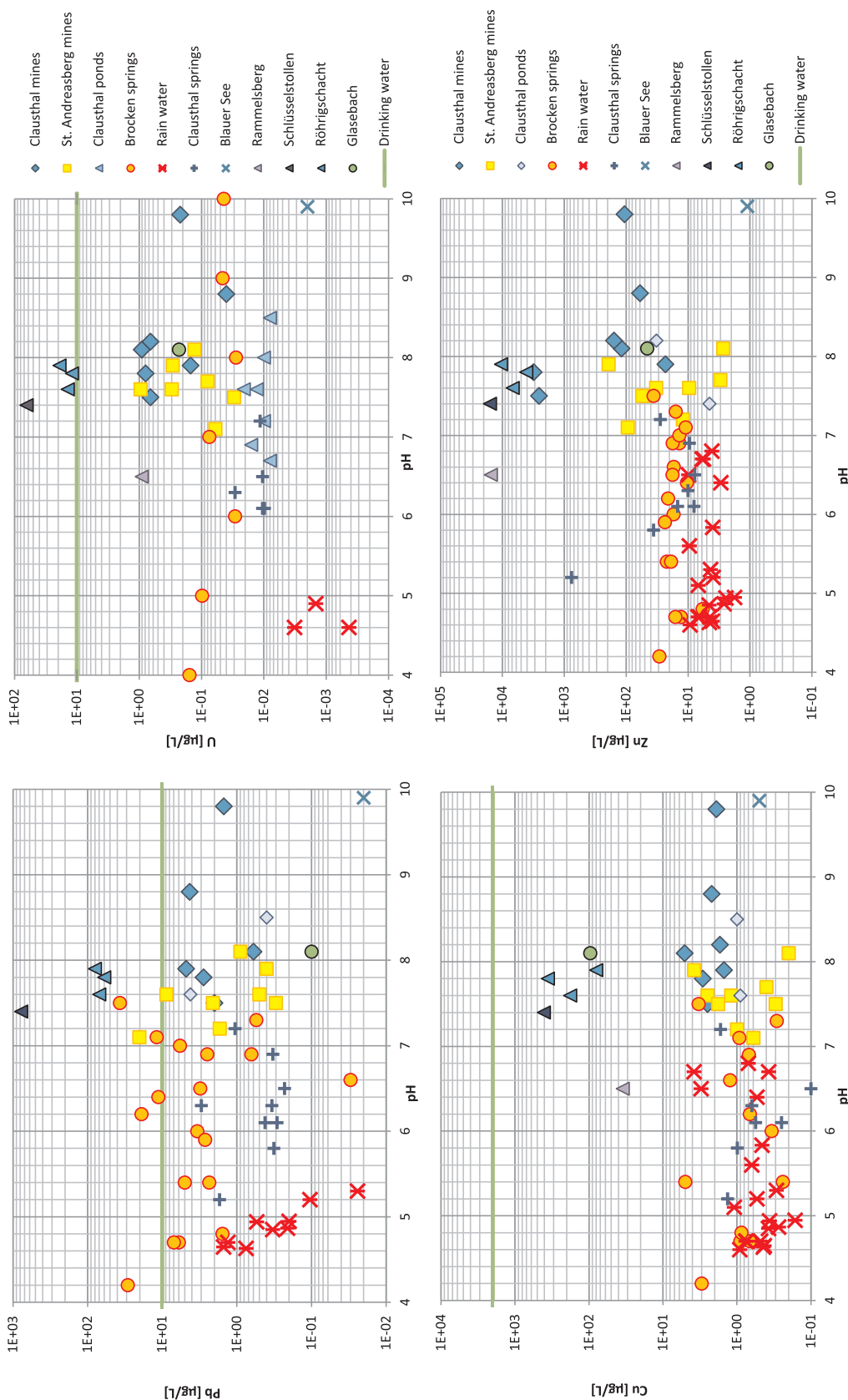


Fig. 8. Lead, uranium, copper and zinc concentrations versus pH values in mine and surface water from the Harz Mountains compared to German limits for drinking water (rain water: personal communication B. Wiegand; spring, lake and creek data: Bozau et al., 2013, 2015a,b,c; Schlüsselstollen: Babrowski and Bozau 2006). The concentrations lower than the detection limits (e.g., most of the U concentrations in rain water) are not considered within the figure. The spring and creek water draining the granitic area around Mount Brocken and the data of the mining ponds around Clausthal can be considered as geogenic background values without ore mineralisation.

To evaluate the hydrogeochemical situation of the Harz Mountains, it is necessary to compare the investigated mine water samples with rain, spring, creek and pond waters. Uranium, lead, zinc and copper concentrations of different waters sampled in the Harz Mountains from 2010 to 2016 are plotted in Fig. 8. The collected data for all trace elements show that there is no correlation between pH value and the trace element concentrations. Trace metal contents of the rain water measured from 2013 to 2014 (pers. communication B. Wiegand) are lower than 1 µg/L for U, and lower than 10 µ/L for Pb and Cu. The Zn concentration of rain water range between 1 and 10 µg/L. Some of the springs, mine pond and mine water samples display Cu, Pb and Zn concentrations in the range of rain water. But compared to rain water, U concentrations are enriched in all other water samples. The highest metal concentrations are found in the waters of the Kupferschiefer district. Due to higher geogenic background values of granitic rocks, all U and some of the measured Pb concentrations are enriched in the waters from the granitic area around Mount Brocken. The measured trace metal and REE concentrations of the ponds around Clausthal are mostly lower than in the granitic area. The geochemical differences of the spring and pond waters caused by water rock interactions, meteoric and anthropogenic influences are discussed in Bozau et al. (2013, 2015b).

Some of the measured metal concentrations (Al, As, Ni, Pb, Sb) in the mine water exceed the German limits for drinking water. Nickel concentrations higher than the limit for drinking water (20 µg/L) are determined in waters from the mines around Clausthal, the mine “Glasebach” and the mine “Röhrigschacht”. The drinking water limit for As (10 µg/L) is exceeded in particular samples of the waters from St. Andreasberg, Clausthal and Wettelrode. In addition to the high As concentrations, the waters sampled in the mines “Fünf Bücher Moses” and “Gnade Gottes” also rise above the drinking water limit for Sb with 5 µg/L. Lead concentrations vary around the value of 10 µg/L in the granitic areas and are considered as geogenic background. The drinking water limit for Pb (10 µg/L) is reached in one sample of the mine district “St. Andreasberg” and in all samples of the mine “Röhrigschacht”.

## 5. Conclusions

The chemical quality of mine waters in the Harz Mountains can be explained by water rock interaction including the leaching of ore minerals in the old mines. Acidification caused by oxidation processes of sulphide minerals was not observed in the investigated mine waters. Because there is a continuous supply of meteoric water to the mines and adits, and near neutral pH values, leached metal concentrations are generally low. Due to the inflow of brines at the deeper, now flooded levels of the mines in the Upper Harz Mountains and the inflow of waters passing Permian salt enriched layers in the Kupferschiefer district southeast of the mountain range, the salinity of these mine waters is further enriched.

Compared to the mine water of the Harz Mountains, the saline water from the Kupferschiefer district is also enriched in trace metals. These high metal concentrations result from the metal enrichments in the Kupferschiefer seam itself and are supported by salting-in effects: rising salt concentrations enhance the metal solubility due to the increased formation of aqueous metal chloride species.

The measured water data do not allow for a definite discrimination between the different ore districts. Only the water from the Kupferschiefer district can be clearly identified by the very high salinity combined with an enrichment of a large trace metal spectrum. There are local differences at the sampling points in the mining districts around Clausthal and St. Andreasberg. But the compositional range within both mining districts is overlapping.

Some metal concentrations of the mine waters from all mining districts in the Middle and Upper Harz Mountains are locally higher than the German limits for drinking water (e.g., As, Ni, Pb). Salinity and trace metal concentrations of mine water in the Kupferschiefer district

generally exceed the limits for drinking water. The high fluoride concentrations measured in the mine “Glasebach” are remediated. To prevent environmental damage, selected parameters of the surface as well as mine waters in the Harz Mountains are regularly monitored by the responsible water management agencies.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemer.2017.10.001>.

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