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Hydrochemical monitoring (1970–2003), depth profile and flow measurements in partly flooded underground workings of the central polymetallic vein ore deposit of Freiberg/Germany*

Hydrochemisches Monitoring (1970–2003), Tiefenprofil- und Strömungsmessungen in teilweise gefluteten Grubenbauen im Zentralteil der polymetallischen Erzlagerstätte Freiberg/Deutschland

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key words: acid mine drainage, flooded mine workings, geochemical barriers, heavy metals, hydraulics, mine water monitoring, seepage water, sulfide oxidation

Abstract

The formation of acid drainage in the abandoned polymetallic sulfide ore mine of Freiberg, Saxony contributes high concentrations of sulfate, arsenic, and heavy metals (Zn, Cd, and Pb) to the Mulde and Triebisch/Elbe Rivers. Former and current studies are based on a more than 33 year long monitoring (5/1970-8/2003), which consists of several investigations and time series. The main goals of the study were the examination and quantification of the processes of mobilisation, transport, and re-fixation of these pollutants, and their enrichment in mine water over several levels in the unflooded and flooded parts of the mine. Quantity and quality of the input seepage water, ground water, and the mixed mine water at the outfall of the flooded mine workings were estimated and a flow model of mine water in the shaft was developed. Mass and element balance calculations (e.g. sulfate, Zn, Na, and Cl) suggest the influx of tailings-influenced seepage water into the flooded part of the mine along the upper levels. Water quality at the outfall significantly improved after the mine was partly flooded in 1971, but the improvement has slowed down considerably since the mid-1990s. Therefore, contaminant concentrations are not expected to decrease significantly during the next decades. In contrast to 1982 and 1997, in 2001/2002, physico-chemical parameters and contaminant concentrations showed little variations in all depths of the flooded shaft. This implies fairly good mixing of the chemically very different influx waters in the flooded part of the mine before the water enters the shaft. Flow measurements also suggest an upward flow along the entire shaft and indicate lateral flow at distinct levels.

Zusammenfassung

Die Grubenwässer aus dem Zentralteil der stillgelegten polymetallischen Erzlagerstätte Freiberg sind eine signifikante Quelle für die Sulfat, Arsen- und Schwermetallbelastung (Zn, Cd, und Pb) des Muldeflußsystems und des deutschen Abschnittes der Elbe. Die Untersuchungen beruhen u. a. auf einem über 33 Jahre laufenden Langzeit-Monitoring (5/1970-8/2003), das sich aus mehreren Untersuchungen und Zeitreihen zusammensetzt. Die Hauptziele dieser Arbeit sind die Untersuchungen der wesentlichen Vorgänge der Elementmobilisierung, des Transportes und der Refixierung dieser Kontaminanten und deren Anreicherung in Grubenwässern in verschiedenen Teufenniveaus im ungefluteten und gefluteten Bereich der Grube. Hierfür wurden Wasserproben von Sicker- und Grundwasser sowie Mischwasser am Überlauf des Grubensystems (Schacht Reiche Zeche) analysiert, Wassermengen abgeschätzt sowie Messungen der Strömungsverhältnisse im Schacht durchgeführt. Massen- und Stoffbilanzen (z. B. Zn, Na, and Cl) deuten auf den Eintrag von tailings-beeinflussten Sickerwässern in dem gefluteten Teil der Grube entlang

* *Dedicated to the memory of Professor Dr. Peter Beuge (11.4.1938 – 21.6. 2001)*

der oberen Sohlenniveaus hin. Die Wasserqualität am Überlauf verbesserte sich nach Teilflutung der Grube 1971 signifikant. Die Schwermetallgehalte nahmen ab. Seit Mitte der 90er Jahre sind nur noch geringfügige Veränderungen zu beobachten. Eine signifikante Verbesserung der Wasserqualität ist in den nächsten Dekaden deshalb nicht zu erwarten. Bei Messungen im gefluteten Reiche-Zeche-Schacht zeigten Messungen der physiko-chemischen Parameter und der Schwermetallbelastung im Gegensatz zu 1982 und 1997 in den Jahren 2001/2002 kaum teufenabhängige Schwankungen. Dies weist auf eine intensive Mischung der in den Flutungsraum eingetragenen chemisch sehr unterschiedlichen Wässer hin. Messungen von Fließrichtungen und -geschwindigkeiten im Reiche-Zeche-Schacht weisen auf ein Aufströmen im gesamten Schacht und auf horizontale Zu- bzw. Abströme auf bestimmten Niveaus hin.

1. Introduction

The Freiberg polymetallic sulfide ore deposit is situated between Dresden and Chemnitz in Saxony, Germany. It is one of the largest vein ore deposits in the world, with more than 30 km N–S extension and more than 1,100 known ore veins. Mining was focused on sulfides such as sphalerite, galena, chalcopyrite, and pyrite, primarily producing Zn, Pb, As, Cu, Ag, and sulfuric acid. The ore mineralisation formed during the Late-variscian and the Post-variscian phase occurs in steeply dipping ore veins of variable orientations, bedded into gneissic wall rock (BAUMANN et al. 2000). The Freiberg mine can be considered as a typical abandoned sulfide mine.

In the central part of the Freiberg deposit (Fig. 1), 800 years of nearly continuous mining to maximum depths of 740 m have created cavities of more than 3.5 million m^3. Between 1968 and 1971, 2.6 million m^3 of mine workings were flooded up to the level of the deepest main adit, the Rothschönberger Stolln, at a depth of about 225 m below the surface. After emerging in the Reiche Zeche shaft at the level of the Rothschönberger Stolln, the mine water mixes with other drainage water and discharges via the Triebisch River into the Elbe River. Another 3.6 m^3/min of mine water drains from the upper unflooded part of the mine via several smaller upper adits into the Mulde River without entering the flooded workings (Fig. 2). Via its three major adits (Rothschönberger Stolln, Hauptstolln Umbruch, Verträgliche Gesellschaft Stolln), the central Freiberg deposit alone yields annually approximately 71 t of Zn, 0.53 t of Cd, 0.19 t of As, and 0.17 t of Pb to the Mulde (BEUGE et al. 1999) and Triebisch/Elbe Rivers. The Freiberg deposit contributes 37 % of the Zn and 5 % of the Cd contamination of the Elbe River (MARTIN et al. 1994).

This study continues a long-term monitoring of more than 33 years (in total) starting in 1970 with data on water chemistry of the flooding water in the shaft and ending one year after the flood in August 2002. In the course of about 8 years (1995-2003) an extensive hydrochemical monitoring at the outfall of the central Freiberg mine together with depth profile and hydraulic measurements in the flooded shaft were carried out. In the past, numerous papers have been published, mainly on various small-scale geochemical processes in water, rock and sediment in the flooded and unflooded part of the mine. On this basis, the major objective of this paper is to show the interaction of such micro- and macro-processes and their importance for the long-lasting high level contaminant output in a typical abandoned sulfide vein ore mine. These processes include contaminant mobilisation, transport, mixing, and re-fixation within the mine, as well as the final discharge of the contaminants via adits and tributaries into the Elbe River. Data interpretation in connection with the results of water quality measurements in the unflooded part of the mine suggest possible hydraulic connections to other contaminant sources and lead to an evaluation of the contaminant potential of this abandoned sulfide ore mine. Due to the complexity of the objective, this paper intensively interlocks already published data (KATZWEDEL 1982, PETER 1983, BAACKE 2000, BAACKE & DEGNER 2000) with new results leading to a new description of the processes in the Freiberg mine.

2. Geological and hydrogeological background: water types and mass balance

The central Freiberg deposit covers an area of 23.7 km^2 (Fig. 1) with a corresponding catchment area of about 34 km^2 without the Morgenstern mine. The average ground water recharge rate can be calculated to be 3.2 L/(s•km^2) with the methods and data of KRAFT & SCHRÄBER (1982), RÖSNER (1987), and BERRIOS (1995), providing ground water formation rates in the range between 2.1 and 3.5 L/(s*km^2) (KOLITSCH 1997). The potential ground water volumes for the catchment area of the central Freiberg mine are 6.6 m^3/min (4.3–7.2 m^3/min). Measurements in the mine and at the outfall (the only discharge point of water from the flooded workings) as well as historical data from the time of mining (CHRONIK 1973) suggest an input and corresponding output of about 2 m^3/min of ground and seepage water each.

Based on a hydrogeological analysis of the mining area and mass balance calculations, water types can be distinguished according to water genesis and migration paths,

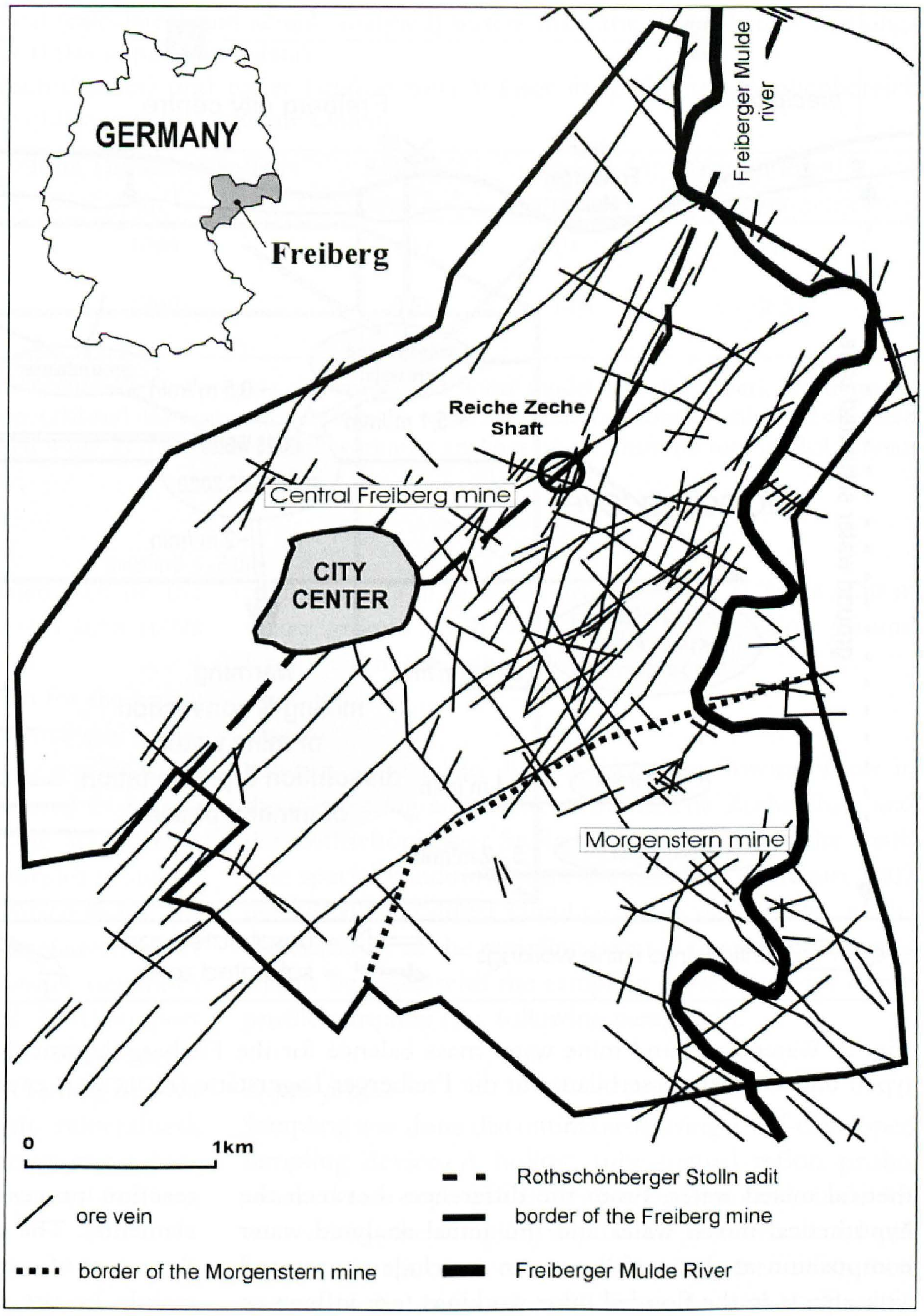


Fig. 1: Locality map of the Freiberg deposit with the position of major ore veins

Abb. 1: Geographische Lage der Freiberger Lagerstätte mit Lage wichtiger Erzgänge

clearly separating seepage and ground water. This was confirmed by numerous analyses of seepage and ground water samples in the unflooded zone (Table 1) and by isotope ratios of S ($\delta^{34}S$) and O ($\delta^{18}O$) in sulfate (KOLITSCH et al. 2001). Though low mineralised, ground water in the Freiberg deposit is still higher mineralised and has $\delta^{34}S_{SO_4}$-values that are clearly affected by sulfide oxidation compared to deposit-distant ground water of the surroundings. Tritium analyses show the highest residence times for ground water and the highly mineralised seepage water (KOLITSCH & JUNGHANS unpublished data). Slow migration rates through joints (ground water) and partially mined vein zones (highly mineralised seepage water) are believed to be responsible. Seepage and ground water enter the flooded mine workings, where they undergo various processes, such as mixing, circulation, reaction, dissolution, and precipitation, and finally flow up the Reiche Zeche shaft (Fig. 2). Residence times of the mine water in the flooded mine workings were estimated to be 100–400 days (BAACKE 2000). About 4 m^3/min of mine water rise in the Reiche Zeche shaft (outfall) and discharge via the adit Rothschönberger Stolln into the Triebisch/Elbe River.

On the basis of the defined properties and quantities of the seepage and ground water entering the flooded part of the mine (Table 1), maximum expected concentrations of the mixed water in the flooded mine workings were estimated. Table 2 shows the characteristics of this hypo-

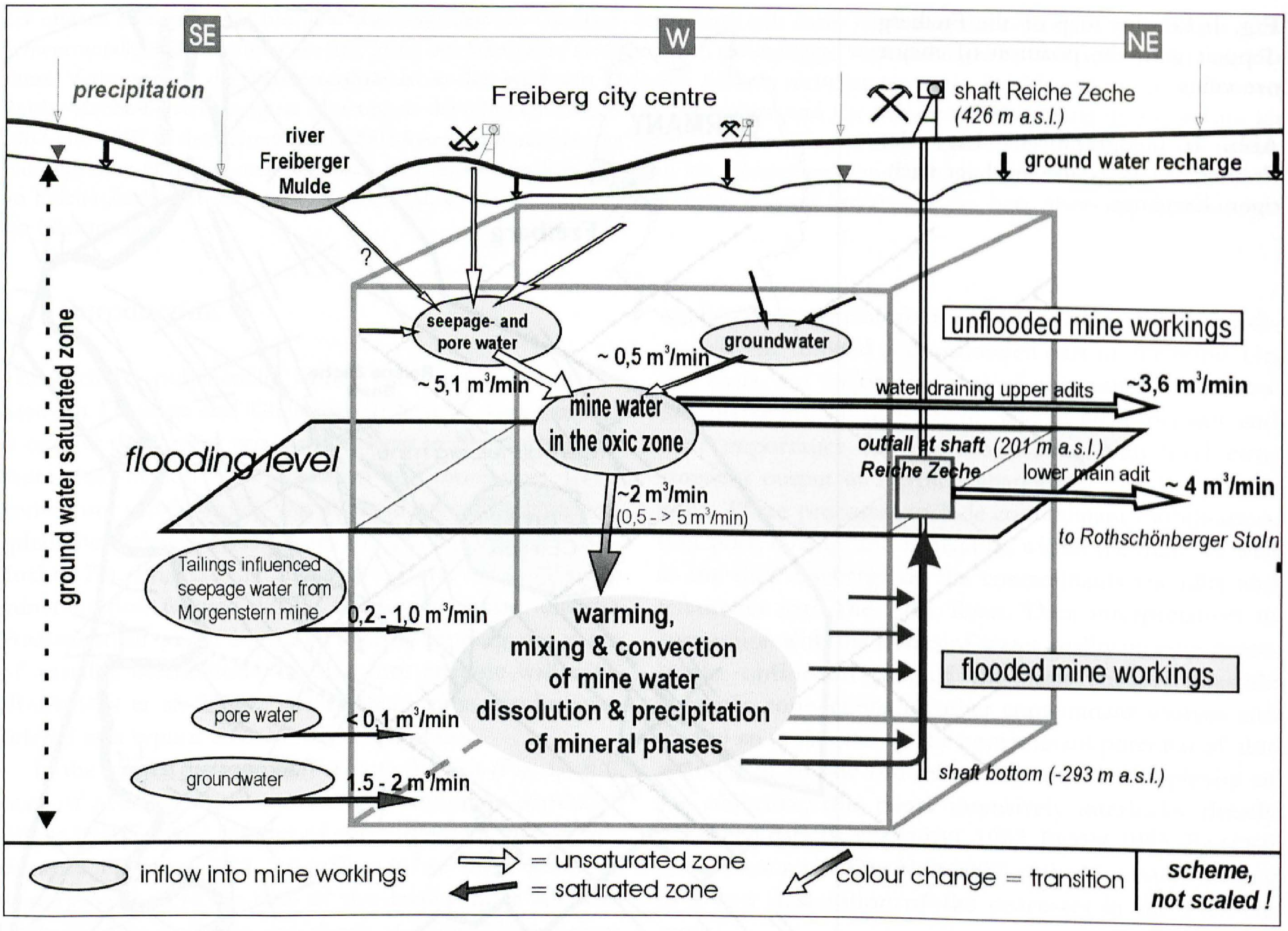


Fig. 2: Water types and mine water mass balance for the Freiberg deposit (KOLITSCH et al. 2001) / **Abb. 2:** Wassertypen und Grubenwasserbilanz für die Freiberger Lagerstätte (KOLITSCH et al. 2001)

thetical mixed water. From the differences between the hypothetical mixed water and the actual analysed water composition at the outfall, we can conclude source and sink effects in the flooded mine workings (e.g. inflows or reaction processes causing mobilisation or fixation of elements). The calculation includes sulfide oxidation to the extent of complete consumption of dissolved oxygen, mainly by ore dissolution including the formation of

Table 1: Characteristics of ground and seepage waters from the unflooded mine workings / **Tab. 1:** Charakteristik der Grund- und Sickerwässer im ungefluteten Grubenbereich

	Quantity m^3/min	Total Dissolved Solids mg/L	Sulfate mg/L	Zinc mg/L	Tritium age* years
Ground water					
rock contact	2 (50 %)	< 500	< 350	< 0.5	≥ 20
ore contact		> 800	> 500	n. a.	
Seepage water					
wall rock contact	1.6 (40 %)	500–1000	< 500	< 20	< 0.5
ore residue contact	0.4 (10 %)	>> 1200	> 1000	< 600	> 14

* mean residence time, calculated from tritium concentrations using dispersion and linear model (ground water), linear model (seepage water with ore residue contact), exponential and dispersion model (seepage water with wall rock contact only) and weighted combinations of the above types for the mixed water in the flooded mine workings; analyses by the Institute for Applied Physics (Detlef Hebert), TU Bergakademie Freiberg
n.a. = not analysed

Table 2: Characteristics of the hypothetical (calculated) and actual (analysed) waters from the flooded mine workings (KOLITSCH et al. 2001, KOLITSCH & JUNGHANS unpublished data)
Tab. 2: Charakteristik hypothetischer (berechneter) und realer (analysierter) Wässer im gefluteten Grubenbereich (KOLITSCH et al. 2001, KOLITSCH & JUNGHANS unveröffentlichte Daten)

	Quantity m^3/min	Total Dissolved Solids mg/L	Sulfate mg/L	Zinc mg/L	Tritium age* years
hypothetical mixed water (calculated)	4	1000	< 400	< 19	10–13
analysed mixed water (discharged)		1700	900	14.4	≥ 5

* mean residence time, calculated from tritium concentrations using dispersion and linear model (ground water), linear model (seepage water with ore residue contact), exponential and dispersion model (seepage water with wall rock contact only) and weighted combinations of the above types for the mixed water in the flooded mine workings; analyses by the Institute for Applied Physics (Detlef Hebert), TU Bergakademie Freiberg

sulfate (e.g. BAACKE 2000), in the flooded part of the mine (KOLITSCH et al. 2001 and KOLITSCH & JUNGHANS unpublished data).

Heavy metal concentrations (here shown for the highly mobile Zn) show a good fit between calculated and actual concentrations. Due to their high mobility Zn and Cd are scarcely fixed and can, in this context, be used as quantitative natural tracer elements. However, the actual mine water is much more mineralised due to a surplus in sulfate (and Ca and Mg) than the hypothetical mixed water. An inflow of highly mineralised water with a relatively short mean residence time is suggested. The isotopic signatures of O and S in the sulfate (KOLITSCH et al. 2001) support the assumption of a hydraulic shortcut to the Morgenstern mine in the southeast of the central Freiberg deposit (Figure 1), causing an inflow of highly mineralised, tailings-influenced seepage water with heavy metal concentrations comparable with those in the central Freiberg mine.

3. Methods

3.1. Sampling, sample treatment, and monitoring technique

3.1.1. Sampling technique

Ground water and seepage water from the unflooded zone

Water samples were taken from a bore hole outside the mine (groundwater, Pegel I – Friedeburg, sampling depth 8.00 m), from drip waters of the fractured gneiss without ore mineralisation (groundwater, Dittersbacher Rösche up to 100 m below ground level (BAACKE 2002)) and from migrating seepage water at different depths of a mined and backfilled ore vein (Schwarzer Hirsch Stehender: Stollnsohle (110 m below ground level), 1. Sohle (150 m below ground level), ½ 3. Sohle (190 m below ground level)) within the mine.

Outfall

Samples were taken directly from the flowing water in the connecting adit between the Reiche Zeche shaft and the Rothschönberger Stolln, just after rising in the shaft. The special conditions after the flooding in August 2002 did not allow a direct sampling at the outfall. Due to the inaccessibilty of the sampling point at the outfall, samples had to be taken with the sampling device used for depth profile sampling (see following paragraph).

Depth profile

Sampling was done discontinuously using a self-developed sampling device. A hollow, tube-shaped teflon probe, attached to a rope was slowly lowered into the shaft. After reaching the sampling depth, the probe remained still for a minimum of 10 minutes to readjust the undisturbed current in the shaft and to fill the probe with a representative sample. Using an automated closing mechanism (falling weight) the device is closed tightly to seal the sample. The probe was then lifted and the enclosed sample treated immediately.

3.1.2. Sample treatment

The physio-chemical parameters (pH, Eh, electrical conductivity, temperature, oxygen concentration) were determined immediately after sampling. For the determination of dissolved Al, As, and heavy metal concentrations, particulate matter was removed by vacuum filtration with a cellulose acetate filter (Sartorius) of a pore size of 0.45 µm, followed by the acidification of the filtered sample with ultra clean HNO_3 (1 ml per 100 ml of sample).

3.1.3. Monitoring technique

Outfall

Since the flooding of the Freiberg mine in the early 70's a discontinuous hydrochemical monitoring at the outfall of the Reiche Zeche shaft was executed. During the beginning of the monitoring (1970-1992), samples were taken at varying time intervals and TDS or electrical conductivity, pH, Ca, SO_4, Fe, Mn, Zn, and partially Na, K, Mg, F, Cl, As, Cd, Cu, and Pb were analysed. In 1995-2003 temperature, electrical conductivity, pH, Eh, O_2, Na, K, Ca, Mg, F, Cl, NO_3, HCO_3, SO_4, and total and dissolved concentrations of Al, As, Cd, Cu, Fe, Mn, Pb, and Zn were determined from samples taken at different time intervals. From 1/1998 to 5/2000 no samples were obtained.

Depth profile

In 1983 (PETER 1983), 1997 (BAACKE 2000, BAACKE & DEGNER 2000), 2000, 2001, and 2002, hydrochemical measurements have been carried out at different depths in the flooded Reiche Zeche shaft. In 1983 pH, electrical conductivity, Na, K, Ca, Mg, F, Cl SO_4, and the total conentrations of As, Cd, Cu, Fe, Mn, Pb, and Zn and from January 1997 additionally temperature, Eh, O_2, the total and dissolved concentrations of Al, the dissolved concentrations of As, Cd, Cu, Fe, Mn, Pb, and Zn and partly Br and Li were measured. Furthermore, continuous measurements of temperature, pH, Eh and dissolved oxygen were accomplished in 1982 (KATZWEDEL 1982), 1997 (BAACKE & DEGNER 2000), and 2002.

3.2. Analysis

The physico-chemical parameters were measured with the following instruments: pH: WTW pH 340, Eh: WTW pH 340, oxygen concentration: WTW Oxi 340, electrical conductivity: WTW LF 340.

Na, K, Mg, and Ca were analysed using F-AAS, HCO_3^- concentration was determined by acidimetric titration and SO_4^-, NO_3^-, and Cl^- concentrations by ion chromatography. The water samples were analysed for Al, As, Cd, Cu, Fe, Mn, Pb, and Zn by ICP-AES, ICP-MS or ETA-AAS depending on their concentration.

3.3. Flow measurements in the Reiche Zeche shaft

On the 25th and 26th of July 2001 flow velocity and continuous high resolution physical parameter measurements were carried out in the Reiche Zeche shaft. Temperature and hydraulic conductivity were measured down to the shaft bottom 470.4 m below outfall. Eh, pH, and oxygen concentration were measured down to 289.2 m below outfall. The results are discussed together with the depth profile measurements.

Discontinuous flow measurements were carried out to analyse flow direction and flow speed in certain depths of the shaft. The measurements -two per depth stage- were performed in depths of 29 m, 89 m, 100 m, 124 m, 161 m, 219 m, 286 m, 297 m, 329 m, 364 m, and 449 m below the outfall. The measurement was done using a heat impulse technique with the flow speed probe HFS 98 by LogIN Bohrlochmessgeräte GmbH, Gommern. First, a defined heat impuls is emitted by the probe and then registered with vertically and horizontally aligned sensors along the probe. In the horizontal direction sensors are arranged in 45° intervals. Travel times based on stream functions and laboratory calibration tests are then calculated. Heating times are 1s for the vertically and 8 s for the horizontally directed flow speed. The detection limits with this method are 1 m/h for the vertical upward, 5 m/h for the vertical downward and 3 m/h for the horizontal flow speed.

4. Results

This section summarises for the first time the results of the authors and previous, mostly unpublished, results (e.g. MILDE 1973, KATZWEDEL 1982, PETER 1983, BAACKE 2000).

4.1. Hydrochemical monitoring of mine related ground and seepage water

4.1.1. Groundwater

Tables 3 a and b show the chemical characteristics of groundwaters in the Freiberg area which are unaffected by ore mineralisation. Groundwaters are characterised by a low electric conductivity, pH values of 5.4 to 6.6, low anion and cation concentrations as well as low Al, As, and heavy metal concentrations.

4.1.2. Mine seepage water

A major seepage water pathway has been examined by WINKLER (1998), BAACKE (2000) and HAUBRICH et al. (2000) at the mined and backfilled ore vein "Schwarzer Hirsch Stehender" from the suspected outcrop at the surface and at different levels of the unflooded zone to investigate the characteristic mobilisation and transport behavior for heavy metals, Al, As, and sulfate. The geo-

Table 3a: Chemical parameters of groundwaters unaffected by ore mineralization / **Tab. 3a:** Chemische Parameter des von Erzmineralisationen unbeeinflussten Grundwassers

Sample	Date	Depth m b.g.l.	Temperature °C	Conductivity µS/cm	pH	Eh mV	O_2 mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	Cl mg/L	NO_3 mg/L	HCO_3 mg/L	SO_4 mg/L
1[1]	3.4.1998	up to 100	–	248	6.3	–	–	7.6	2.0	23.1	8.3	5.5	44.2	15	45
2[1]	3.4.1998	up to 100	–	268	6.1	–	–	7.6	1.8	22.4	10.7	6.6	48.5	16	42
3[1]	3.4.1998	up to 100	–	314	6.6	–	–	8.9	1.4	33.7	9.7	7.9	49.2	41	47
4[2]	2002	unknown	10.9	387	5.7	428	8.1	16.3	2.3	43.0	11.2	25.4	18.0	13	120
5[3]	25.7.2002	15	11.7	50.3	5.4	566	6.2	7.4	1.4	20.1	6.2	9.4	24.2	8	58

m b.g.l. = m below ground level

Table 3b: Al, As and heavy metal concentration of groundwaters unaffected by ore mineralization / **Tab. 3b:** Al-, As- und Schwermetallkonzentration des von Erzmineralisationen unbeeinflussten Grundwassers

Sample	Al mg/L	As mg/L	Cd mg/L	Cu mg/L	Fe mg/L	Mn mg/L	Pb mg/L	Zn mg/L
1[1]	0.0198	0.0017	0.00015	0.0053	0.005	0.002	0.002	0.0056
2[1]	0.0142	0.0020	0.00005	0.0010	0.005	0.001	0.001	0.0020
3[1]	0.0104	0.0049	0.0001	0.0010	0.005	0.001	0.001	0.0006
4[2]	–	< 0.001	0.0012	–	0.002	0.63	–	0.0011
5[3]	0.0293	bdl	0.0025	0.0035	0.075	0.019	0.041	0.0043

[1] BAACKE 2000 Dittersbacher Rösche, barren gneiss   bdl = below detection limit
[2] VOLKE 2001
[3] sample provided by SCHULZE & KLEEBERG, IHS consulting company

Table 4: Analytical results of the migrating seepage water at a mined ore vein (BAACKE unpublished data, WINKLER 1998) (sample point 1 is groundwater from a borehole above the assumed outcrop of the ore vein) (Sample point 1: data are mean values of six sampling campaigns; sample points 2-6: sampling date 29.4.1997)
Tab. 4: Analytische Ergebnisse der Sickerwässer eines abgebauten Erzganges (BAACKE unveröffentlichte Daten, WINKLER 1998) (Probenahmepunkt 1 ist Grundwasser eines Bohrloches über dem vermuteten Ausbiss des Erzganges) (Probenahmepunkt 1: Daten sind Durchschnittswerte von sechs Probenahmen; Probenahmepunkte 2-6: Probenahmedatum 29.04.1997)

Sample point	Conductivity µS/cm	pH	Eh mV	O_2 mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	Cl mg/L	HCO_3 mg/L	SO_4 mg/L	NO_3 mg/L	Al mg/L	As mg/L	Cd mg/L	Cu mg/L	Fe mg/L	Mn mg/L	Pb mg/L	Zn mg/L
1	427	5.6	457	8.2	14.3	11.30	39.5	13.3	15.5	9.0	139	28.9	0.404	0.007	0.017	0.026	0.13	2.142	0.019	1.66
2	441	5.6	592	10.3	10.3	3.43	43.1	16.4	14.5	27.5	140	44.0	0.202	0.005	0.020	0.015	0.01	0.223	0.120	2.33
3	444	5.6	600	10.2	10.5	3.47	44.1	16.4	15.8	18.3	171	50.2	0.335	0.010	0.021	0.028	0.09	0.230	0.065	2.43
4	477	4.2	695	10.1	10.5	3.42	45.1	16.4	14.4	0.0	150	49.3	0.474	0.006	0.040	0.09	0.40	0.337	0.369	4.10
5	491	4.1	692	10.0	10.3	3.41	45.1	17.0	14.9	0.0	161	44.9	0.641	0.024	0.054	0.08	1.1	0.397	0.358	4.94
6	565	3.7	755	9.9	10.5	3.24	47.1	17.6	15.5	0.0	166	40.2	1.270	0.010	0.094	0.17	1.0	0.627	0.517	7.85

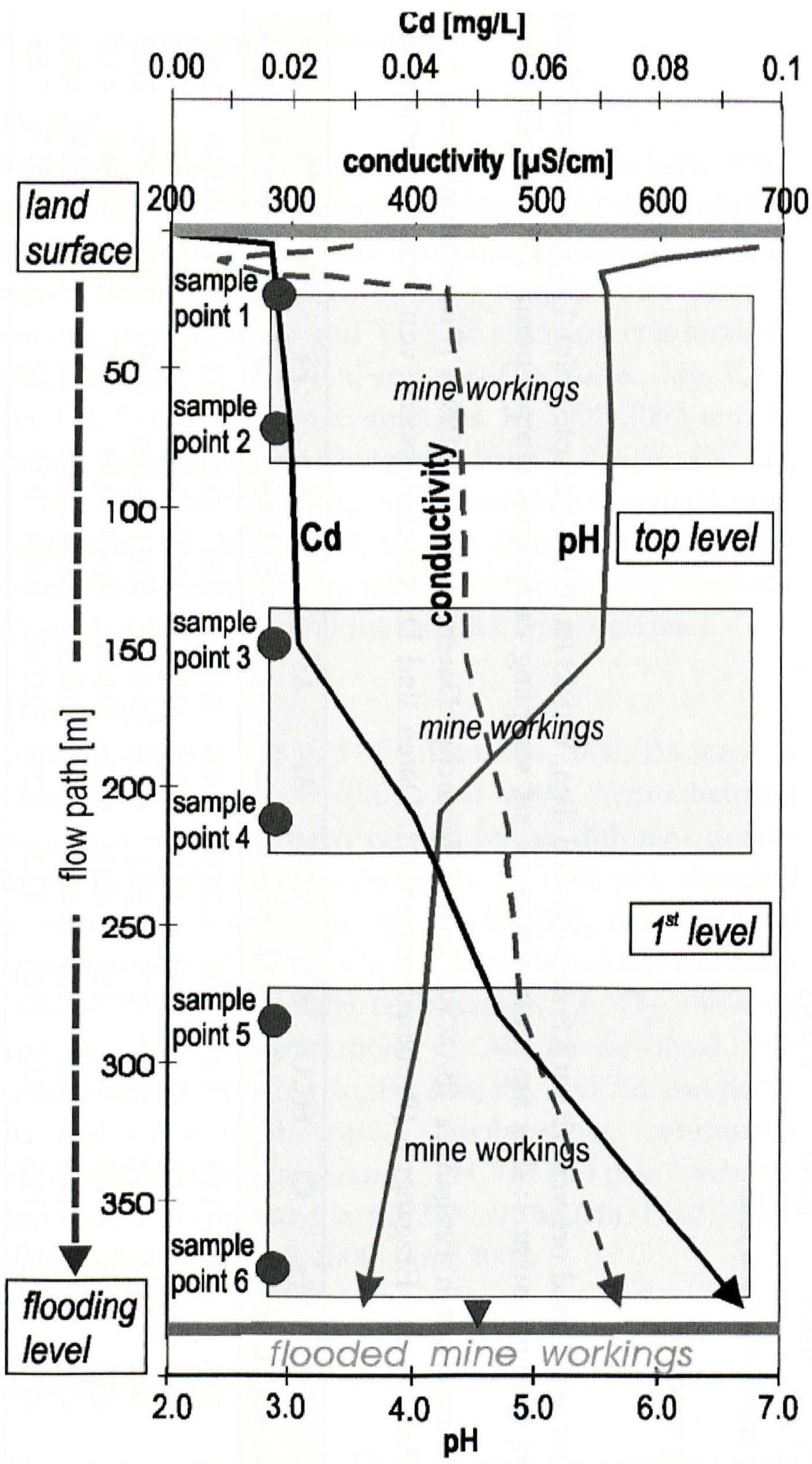


Fig. 3: Selected hydrochemical parameters in seepage waters of the unflooded mine workings (modified after BAACKE 2000)

Abb. 3: Ausgewählte hydrochemische Parameter in Sickerwässern des ungefluteten Grubenraumes (modifiziert nach BAACKE 2000)

chemical characteristics of the water at different depths is given in table 4.

Sampling point 1 is a groundwater taken at the suspected outcrop of the backfilled ore vein "Schwarzer Hirsch Stehender". A comparison with groundwaters unaffected by ore mineralisation exhibits higher concentrations for K, Mg, SO_4, Al, As, Cd, Cu, Fe, Mn, and Zn for sampling point 1. Seepage water from a nearby waste rock dump might be causing the elevated concentrations (WINKLER 1998).

Along the flow path from sampling point 2 to sampling point 6 an increase in electric conductivity, a decrease in pH, and a strong increase in Al, Cd, Fe, Mn, and Zn can be observed. Figure 3 shows the development of electric conductivity, pH, and Cd concentration along the flow path.

4.1.3. Pore waters of weathered vein ore material

The complex weathering processes produce soluble components as well as secondary phases (e.g. jarosite, scorodite, illite). The clayey material (so called "Letten") exhibits a high pore water content and pore waters with a high acidity as well as high heavy metal concentrations (BAACKE 2000, TICHOMIROWA et al. 2003) (Table 5).

4.2. Hydrochemical monitoring of the Reiche Zeche shaft

Tables 6a–c show the results of the hydrochemical monitoring of the mine water rising at the Reiche Zeche shaft between 1970 and 2003. They show the development of

Table 5: Chemical composition of pore water extracted from weathered vein ore material (data from TICHOMIROWA et al. 2003) / **Tab. 5:** Chemische Zusammensetzung von Porenwasser aus verwittertem Gangerzmaterial (Daten aus TICHOMIROWA et al. 2003)

Sample	Colour	H_2O content %	pH	SO_4 g/L	Al mg/L	As mg/L	Cd mg/L	Cu mg/L	Fe mg/L	Mn mg/L	Pb mg/L	Zn mg/L	Primary ore mineralisation
P1	yellow brown	18.2–20.8	2.0–2.3	4.75–14.7	80.9–353	<0.075–4.5	11.2–48.3	5.0–35.6	850–5130	137–752	–	1100–6170	galena, sphalerite, pyrite>>arsenopyrite
P2	grey green	17.4	1.1	54.6–107	18–1240	390–8640	13.5–22.5	15.2–49.6	850–25250	66–109	78.7–162	1863–3390	arsenopyrite, pyrite>galena, sphalerite

water quality in the flooded mine workings in the central part of the Freiberg mining district. The sample of May 1970 was taken from the rising water before flooding was completed.

In general, a continuous decrease of deposit-related mineralisation since flooding in 1971 was observed. Total dissolved solids dropped from about 7,500 mg/L in 1971 to about 1300 mg/L in summer 2003. However, the dynamics of the mineralisation decrease is slowing down. The pH increased from 3.7 to around 6, where it has stabilised since 1995 (Figure 4). Temperature sank from 22.5°C in 1982 to less than 17°C in 1995 and then rose again to a constant 19°C today. The concentration of Na and Cl decreased between 1997 and 2000, whereas the proportion of both components was changed (Figure 4). Since 1985, only a moderate drop has been observed in most deposit-related element concentrations. Sulfate concentrations (Figure 5) and total Cd concentrations in the first seven months of 2002 were about 65-75% and about 50–80%, respectively, of those recorded in 1985. Between 1996 and 2002 Ca and sulfate vary only slightly at 300 mg/l and 1.000 mg/l, respectively. Since 1997, Cd, Cu, Mn, and Zn concentrations have not changed considerably. The concentration of dissolved Fe decreased since 2001 (Figure 6).

During the flood event in August 2002, between 20 and 30% of the unflooded part of the mine workings (several hundred thousand m^3) were flushed and temporarily flooded. Large amounts of highly mineralised solutions, products of oxidation processes lasting for hundreds of years, were flushed out and mixed with the mine water in the flooded mine workings. The flood event (indicated by an arrow in Figure 6) caused an increase particularly of heavy metal, Al and As concentrations in the drainage (KOLITSCH et al. 2003). By August 2003 conditions had largely returned back to the state before the flood. The Mn concentration, however, is an exception: Mn concentration decreased significantly between 70 and 178 days after the flood event. In August 2003, one year after the flood event, the Mn concentration is still about 43% of the pre-flood concentration.

4.3. Depth profile measurements of the Reiche Zeche shaft

In general, measurements performed in the flooded Reiche Zeche shaft between 1983 and 2002 showed a decrease in deposit-related contaminant concentrations in correspondence to the outfall. In 1983, these concentrations (e.g. Zn, Cd, Pb, As, Ca, sulfate) showed a discontinuous increase with depth (Tables 7–14). Maximum concentrations and minimum Zn/Cd ratios (see below)

Table 6a: Physico-chemical parameters of mine water at the outfall (Reiche Zeche shaft) / **Tab. 6a:** Physiko-chemische Parameter des Grubenwassers am Überlauf (Reiche-Zeche-Schacht)

Date	T °C	*(TDS) mg/L* Conductivity µS/cm	pH	Eh mV	O_2 mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	F mg/L	Cl mg/L	NO_3 mg/L	HCO_3 mg/L	SO_4 mg/L
15.05.70[1*]	–	*(8985)*	4.0	–	–	–	–			–	52	–	–	4910
15.04.71[1]	–		4.8	–	–	–	–	345	–	–		–	–	3000
15.06.71[1]	–	*(7590)*	4.4	–	–	–	–	695	–	–	53	–	–	4590
15.08.71[1]	–	*(8170)*	3.7	–	–	–	–	437	–	–		–	–	3800
15.10.71[1]	–	*(6120)*	3.9	–	–	–	–	428	–	–		–	–	3610
15.01.72[1]	–	*(5840)*	4.1	–	–	–	–	428	–	–	142	–	–	3490
15.03.72[1]	–	*(5980)*	4.1	–	–	–	–	392	–	–	–	–	–	–
15.04.72[1]	–	*(5820)*	4.5	–	–	–	–	392	–	–	31	–	–	3300
15.10.72[1]	–	*(5240)*	3.8	–	–	–	–	378	–	–	16	–	–	3120
23.02.83[2]	–	–	5.8	–	–	64	18.0	512	59.9	2.40	258	<1	–	1454
19.04.85[2]	–	2246	5.9	–	–	61	16.8	486	56.8	1.10	255	<1	–	1336
01.03.92[3]	–	–	–	–	–	–	–	–	–	–	–	–	–	1193
10.02.95[4]	16.8	–	5.8	383	2.8	351	20.6	253	58.4	–	320	–	132	860
15.02.95[4]	16.7	3250	6.1	388	1.9	368	21.0	269	61.8	–	335	–	118	835
27.04.95[4]	15.2	3410	6.1	419	7.0	388	21.8	273	59.3	–	410	5.0	137	800
22.08.95[4]	18.1	3300	6.2	407	1.9	357	13.5	260	45.0	2.45	274	–	142	1308
04.10.95[4]	18.0	3650	6.1	287	–	376	19.4	103	27.4	6.00	256	3.4	87	1114
07.11.95[4]	18.4	3260	6.3	498	–	400	19.4	179	35.9	6.00	230	2.2	82	1100
25.01.96[4]	18.3	3110	6.3	345	1.7	340	17.0	309	61.4	0.05	224	8.2	95	1273
13.03.96[4]	17.5	2810	6.1	737	9.9	250	16.1	264	72.5	–	203	5.6	84	1114
01.04.96[4]	17.6	2680	5.9	373	1.9	222	24.0	250	37.9	0.05	210	3.6	51	1140
04.06.96[4]	17.6	2560	–	259	1.5	–	–	–	–	–	–	–	–	–
07.01.97[4]	18.3	2890	6.1	344	1.2	246	16.6	291	56.4	0.05	243	3.0	104	1184
08.01.97[4]	18.0	2830	6.2	355	2.2	236	15.7	290	57.0	0.05	232	4.8	103	1164
09.01.97[4]	18.0	2850	6.1	362	1.3	241	15.9	292	57.4	1.94	244	2.2	106	1200
21.01.97[4]	18.0	2760	6.2	–	1.3	244	15.1	288	58.3	0.05	242	2.4	100	1313
04.02.97[4]	18.0	2790	5.9	376	1.2	277	16.2	285	58.3	1.76	219	2.0	109	1180
17.02.97[4]	17.8	2840	6.1	352	0.8	284	16.5	287	61.7	0.05	214	2.2	103	1198
24.02.97[4]	18.2	2740	6.2	347	1.4	–	–	–	–	–	–	–	–	–
03.03.97[4]	17.8	2680	6.3	362	1.6	259	15.9	280	58.3	0.73	240	4.0	93	1247
14.03.97[4]	18.0	2700	6.1	362	1.2	263	16.1	285	58.3	2.20	229	2.4	–	1223
26.03.97[4]	17.9	2660	5.5	366	1.8	256	16.0	280	58.8	0.05	230	5.8	82	1225
11.04.97[4]	18.0	2660	6.0	390	1.3	252	16.0	281	63.2	3.20	233	2.8	93	1228
29.04.97[4]	18.2	2680	6.1	380	0.9	234	16.3	288	59.3	0.05	217	0.1	98	1208
12.05.97[4]	18.1	2660	6.1	365	1.0	223	15.9	283	61.8	0.05	177	4.6	105	1032
26.05.97[4]	18.2	2660	6.1	336	0.9	257	16.0	289	60.3	0.05	225	2.7	108	1255
09.06.97[4]	18.5	2660	6.1	340	0.8	251	15.8	293	53.0	2.40	210	0.1	105	1280
20.06.97[4]	18.2	2650	6.1	–	0.8	249	15.7	289	60.8	5.10	202	2.2	102	1090
07.07.97[4]	18.5	2610	6.2	–	0.7	238	15.9	292	57.4	1.12	217	3.6	96	1440
22.07.97[4]	18.5	2580	5.9	–	0.7	242	15.9	283	58.8	2.20	194	8.4	87	1120
01.08.97[4]	18.4	2570	6.1	–	0.9	196	32.2	273	50.4	2.30	182	9.0	–	1080
28.08.97[4]	19.0	2690	6.1	–	0.8	242	33.0	314	54.0	3.00	201	0.1	104	1120
19.09.97[4]	19.1	2640	6.1	–	0.4	250	30.0	320	50.0	2.70	197	0.1	–	1120
01.10.97[4]	19.1	2620	6.1	328	0.4	230	33.0	320	54.0	2.80	195	0.1	101	1090
13.10.97[4]	19.1	2650	6.1	–	0.4	240	34.0	322	55.0	3.20	195	0.1	101	1100
27.10.97[4]	19.2	2640	6.1	331	0.3	225	33.0	320	56.0	3.10	191	0.1	106	1120
11.11.97[4]	18.9	2590	6.1	348	0.5	220	30.0	320	55.0	2.30	189	0.1	110	1080
26.11.97[4]	18.7	2630	6.1	–	0.3	215	15.5	305	58.3	0.05	207	0.1	111	1113
08.12.97[4]	18.7	2600	6.1	313	0.3	211	15.3	303	59.5	0.05	181	–	110	1011
19.12.97[4]	18.7	2600	6.2	322	0.5	211	15.7	299	63.2	0.05	134	0.1	134	1110
20.06.00	19.1	2010	6.0	–	0.2	111	12.2	289	64.2	3.17	137	2.6	24	904
21.11.00	19.0	1717	6.1	445	0.2	–	–	–	–	–	–	–	–	–
07.12.00	19.1	1791	6.1	445	0.0	100	11.6	306	54.6	–	135	bdl	–	906
16.01.01	–	–	–	–	–	106	11.7	308	53.5	–	145	bdl	87	854
23.01.01	17.9	1812	6.2	344	–	93	12.1	365	59.0	2.10	132	–	105	960
01.02.01[5]	19.1	2222	–	–	–	–	–	–	–	–	–	–	–	–
02.02.01	19.1	1947	6.2	416	0.8	101	12.6	301	63.2	–	128	bdl	103	899
07.03.01	19.1	2040	6.1	426	3.9	100	12.1	295	55.1	–	135	bdl	–	941
15.03.01	19.1	2050	6.1	445	0.5	100	12.2	299	54.5	1.64	130	bdl	–	966
10.04.01	19.0	2247	6.1	569	–	96	9.5	320	52.0	–	130	–	103	930
08.06.01	19.1	1970	6.1	431	–	103	12.0	309	48.8	1.08	140	0.4	–	964

Table 6a continued

Date	T	(TDS) mg/L Conductivity	pH	Eh	O_2	Na	K	Ca	Mg	F	Cl	NO_3	HCO_3	SO_4
	°C	µS/cm		mV	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
24.07.01	19.1	1950	6.1	475	0.3	97	12.3	290	53.5	0.76	138	4.2	–	960
02.11.01	18.9	2090	6.1	445	0.2	88	12.0	295	54.0	1.93	134	bdl	75	928
22.11.01	19.1	1929	6.0	550	0.4	91	11.7	297	56.3	2.08	131	bdl	76	968
11.12.01	19.1	1979	6.0	482	0.3	94	11.7	270	52.0	1.65	134	bdl	76	915
15.01.02	19.1	1866	6.1	477	0.3	89	11.5	292	56.0	1.17	128	bdl	122	907
24.01.02	19.1	1869	6.0	460	0.4	88	11.7	294	49.5	1.58	133	bdl	51	973
11.02.02	19.0	1855	6.1	308	0.3	–	–	–	–	1.42	128	bdl	91	943
12.03.02	19.0	1812	6.1	489	0.5	85	11.8	281	51.6	1.35	128	1.6	89	922
04.04.02	19.0	1807	6.1	472	0.3	87	12.3	283	52.5	1.93	129	3.7	78	862
16.04.02	19.0	1678	6.1	486	0.3	84	12.2	279	51.6	bdl	125	1.7	72	848
30.04.02	19.0	1920	6.0	496	0.3	84	12.1	276	51.2	1.01	130	6.8	71	887
30.05.02	19.0	1882	6.1	473	0.4	85	10.5	289	52.7	1.49	128	bdl	86	953
28.06.02	18.7	1940	6.1	462	0.8	84	10.7	287	53.3	1.85	125	bdl	88	920
16.07.02	19.0	1864	6.1	465	0.5	85	10.3	290	52.7	1.62	126	bdl	72	935
23.07.02	19.0	1887	6.2	435	0.7	83	10.2	289	53.8	1.70	128	bdl	77	951
06.08.02	–	1942	6.1	576	0.5	83	11.5	302	53.0	1.79	129	bdl	86	974
11.09.02	18.0	1664	5.9	519	4.2	73	10.8	267	48.8	2.33	103	7.2	51	920
27.09.02	18.2	1760	6.1	479	4.1	73	11.0	285	51.1	0.62	111	2.9	68	844
22.10.02	16.6	1890	6.0	493	5.5	69	11.2	253	46.8	1.07	108	3.3	–	794
07.02.03	17.7	1333	6.0	474	4.2	53	9.5	201	39.8	1.57	88	4.6	65	735
25.06.03	17.4	1469	6.1	511	3.2	51	10.1	204	40.5	2.26	89	3.5	74	679
24.08.03	18.4	1354	6.1	467	2.9	57	10.5	209	43.0	1.20	94	1.1	71	748

[1] MILDE 1973, * before complete flooding
[2] PETER 1983
[3] HAUBRICH 2001
[4] BAACKE 2000
[5] WOLKERSDORFER written communication
bdl = below detection limit

Table 6b: Al, As and heavy metal concentrations of the mine water at the outfall (Reiche Zeche shaft) / **Tab. 6b:** Al, As und Schwermetallkonzentrationen im Grubenwasser am Überlauf (Reiche-Zeche-Schacht)

Date	Al tot mg/L	Al diss mg/L	As tot mg/L	As diss mg/L	Cd tot mg/L	Cd diss mg/L	Cu tot mg/L	Cu diss mg/L
15.05.70[1]*	–	–	–	–	–	–	–	–
15.04.71[1]	–	–	–	–	–	–	–	–
15.06.71[1]	–	–	–	–	–	–	–	–
15.08.71[1]	–	–	–	–	–	–	–	–
15.10.71[1]	–	–	–	–	–	–	–	–
15.01.72[1]	–	–	–	–	–	–	–	–
15.03.72[1]	–	–	–	–	–	–	–	–
15.04.72[1]	–	–	–	–	–	–	–	–
15.10.72[1]	–	–	–	–	–	–	–	–
23.02.83[2]	–	–	–	–	–	–	–	–
19.04.85[2]	–	–	0.600	–	0.110	–	0.035	–
01.03.92[3]	–	–	–	–	–	–	–	–
10.02.95[4]	–	–	0.003	0.003	0.070	0.069	0.074	0.050
15.02.95[4]	–	–	0.010	0.010	0.057	0.054	0.048	0.040
27.04.95[4]	–	–	0.002	0.002	0.061	0.061	–	0.037
22.08.95[4]	–	–	–	0.001	–	0.125	–	0.050
04.10.95[4]	–	0.43	–	0.001	–	0.015	–	0.048
07.11.95[4]	–	0.77	–	0.017	–	0.082	–	0.082
25.01.96[4]	–	1.90	0.020	0.020	0.190	0.189	0.140	0.123
13.03.96[4]	–	–	–	–	–	–	–	–
01.04.96[4]	0.72	0.52	0.024	0.001	0.126	0.117	0.047	0.028
04.06.96[4]	–	–	–	–	–	–	–	–
07.01.97[4]	0.76	0.52	0.084	0.003	0.068	0.068	0.046	0.033
08.01.97[4]	1.47	0.97	0.081	0.003	0.084	0.083	0.061	0.044
09.01.97[4]	0.63	0.31	0.086	0.003	0.073	0.072	0.042	0.027
21.01.97[4]	1.21	0.71	0.071	0.003	0.107	0.106	0.064	0.049
04.02.97[4]	0.82	0.60	0.076	0.003	0.066	0.066	0.076	0.065
17.02.97[4]	0.97	0.71	0.075	0.003	0.069	0.069	0.079	0.070
24.02.97[4]	–	–	–	–	–	–	–	–
03.03.97[4]	0.82	0.66	0.035	0.002	0.075	0.075	0.084	0.079

Table 6b continued

Date	Al tot mg/L	Al diss mg/L	As tot mg/L	As diss mg/L	Cd tot mg/L	Cd diss mg/L	Cu tot mg/L	Cu diss mg/L
14.03.97[4]	0.99	0.69	0.068	0.002	0.076	0.076	0.095	0.083
11.04.97[4]	1.02	0.67	0.062	0.001	0.078	0.078	0.090	0.078
29.04.97[4]	0.83	0.65	0.051	0.001	0.070	0.069	0.080	0.071
12.05.97[4]	0.82	0.71	0.024	0.001	0.072	0.072	0.077	0.072
26.05.97[4]	0.59	0.49	0.052	0.001	0.065	0.065	0.063	0.057
09.06.97[4]	0.56	0.41	0.055	0.001	0.067	0.067	0.063	0.056
200.6.97[4]	0.72	0.55	0.060	0.003	0.062	0.062	0.067	0.059
07.07.97[4]	0.98	0.73	0.064	0.002	0.078	0.077	0.076	0.065
22.07.97[4]	0.68	0.58	0.027	0.001	0.077	0.077	0.029	0.024
01.08.97[4]	0.87	0.69	0.075	0.017	0.084	0.083	0.044	0.035
18.08.97[4]	0.44	0.35	0.060	0.002	0.047	0.047	0.020	0.015
28.08.97[4]	0.26	0.23	0.052	0.003	0.042	0.042	0.010	0.008
19.09.97[4]	0.23	0.21	0.041	0.002	0.063	0.063	0.007	0.005
01.10.97[4]	0.21	0.19	0.020	0.001	0.058	0.058	0.007	0.006
13.10.97[4]	0.23	0.21	0.046	0.001	0.061	0.061	0.012	0.009
27.10.97[4]	0.29	0.26	0.044	0.001	0.061	0.061	0.008	0.006
11.11.97[4]	0.28	0.19	0.047	0.002	0.049	0.049	0.012	0.010
26.11.97[4]	0.23	0.22	0.054	0.005	0.048	0.048	0.013	0.011
08.12.97[4]	0.20	0.20	0.025	0.001	0.055	0.055	0.006	0.005
19.12.97[4]	0.21	0.19	0.053	0.002	0.054	0.054	0.014	0.012
20.06.00	–	–	–	–	–	–	–	–
21.11.00	–	–	–	–	–	–	–	–
07.12.00	–	0.33	–	bdl	–	0.067	–	bdl
16.01.01	–	–	–	–	0.062	0.063	–	–
23.01.01	–	0.43	–	0.001	–	0.060	–	0.010
01.02.01[5]	–	–	–	–	–	–	–	–
02.02.01	–	0.32	0.097	0.029	–	0.069	–	0.003
07.03.01	0.311	0.44	0.033	0.004	0.061	0.075	bdl	bdl
15.03.01	0.765	0.23	0.055	0.023	0.079	0.069	0.030	bdl
10.04.01	–	0.32	–	0.002	–	0.055	–	0.010
08.06.01	–	0.34	–	0.004	–	0.068	–	bdl
24.07.01	0.420	0.29	0.031	0.007	0.073	0.071	0.017	0.011
02.11.01	0.554	0.37	0.041	bdl	0.087	0.084	0.028	0.032
22.11.01	0.368	0.29	–	bdl	0.060	0.050	0.009	0.014
11.12.01	0.444	0.38	bdl	bdl	0.092	0.062	0.020	0.009
15.01.02	0.536	0.45	0.024	bdl	0.068	0.068	0.038	0.028
24.01.02	0.342	0.27	0.023	bdl	0.053	0.051	0.015	0.012
11.02.02	0.447	0.39	0.040	0.025	0.076	0.072	0.037	0.022
12.03.02	0.264	0.28	0.020	0.006	0.091	0.095	0.021	0.022
04.04.02	0.445	0.42	bdl	bdl	0.082	0.086	0.029	0.024
16.04.02	0.328	0.30	bdl	bdl	0.073	0.037	0.029	0.025
30.04.02	0.335	0.37	bdl	bdl	0.070	0.082	0.026	0.026
30.05.02	0.280	0.27	0.017	bdl	0.065	0.069	0.018	0.015
28.06.02	0.028	0.28	0.022	0.005	0.058	0.065	0.017	0.014
23.07.02	0.300	0.30	0.016	0.003	0.074	0.073	0.016	0.013
06.08.02	0.330	0.31	0.022	bdl	0.081	0.078	0.021	0.034
11.09.02	1.030	0.86	0.027	bdl	0.169	0.169	0.061	0.053
27.09.02	0.800	0.69	0.003	0.0001	0.155	0.152	0.059	0.041
22.10.02	0.697	0.53	0.126	0.005	0.126	0.123	0.044	0.034
07.02.03	0.560	0.49	0.089	bdl	0.130	0.130	0.040	0.031
01.03.03	0.580	0.52	0.053	0.003	0.130	0.130	0.032	0.029
25.06.03	0.490	0.42	0.078	0.004	0.112	0.122	0.028	0.021
24.08.03	0.408	0.33	0.006	0.004	0.103	0.101	0.023	0.015

1 MILDE 1973, * before complete flooding
2 PETER 1983
3 HAUBRICH 2001
4 BAACKE 2000
5 WOLKERSDORFER written communication

bdl = below detection limit
diss = dissolved concentration
tot = total concentration

Table 6c: Heavy metal concentrations and Zn/Cd ratios at the outfall (Reiche Zeche shaft) / **Tab. 6c:** Schwermetallkonzentrationen und Zn/Cd-Verhältnisse im Grubenwasser am Überlauf (Reiche-Zeche-Schacht)

Date	Fe tot mg/L	Fe diss mg/L	Mn tot mg/L	Mn diss mg/L	Pb tot mg/L	Pb diss mg/L	Zn tot mg/L	Zn diss mg/L	Zn/Cd ratio
15.05.70[1]*	520	–	250	–	–	–	–	–	–
15.04.71[1]	590	–	240	–	–	–	525	–	–

Table 6c continued

Date	Fe tot mg/L	Fe diss mg/L	Mn tot mg/L	Mn diss mg/L	Pb tot mg/L	Pb diss mg/L	Zn tot mg/L	Zn diss mg/L	Zn/Cd ratio
15.06.71[1]	542	–	–	–	–	–	630	–	–
15.08.71[1]	337	–	1750	–	–	–	517	–	–
15.10.71[1]	467	–	1500	–	–	–	520	–	–
15.01.72[1]	434	–	215	–	–	–	492	–	–
15.03.72[1]	434	–	200	–	–	–	452	–	–
15.04.72[1]	470	–	122	–	–	–	422	–	–
15.10.72[1]	475	–	226	–	–	–	306	–	–
23.02.83[2]	–	–	–	–	–	–	–	–	–
19.04.85[2]	51.5	–	22.0	–	0.015	–	27.0	–	245
01.03.92[3]	–	–	–	–	–	–	–	–	–
10.02.95[4]	2.78	0.28	10.8	10.8	0.064	0.004	12.6	12.5	181
15.02.95[4]	1.62	0.22	11.1	11.1	0.052	0.006	12.0	12.0	222
27.04.95[4]	0.92	0.05	10.3	10.3	0.091	0.061	13.0	13.0	213
22.08.95[4]	–	0.08	–	9.9	–	0.070	–	15.9	127
04.10.95[4]	–	1.76	–	2.3	–	0.005	–	2.1	141
07.11.95[4]	–	0.35	–	9.0	–	0.034	–	13.4	163
25.01.96[4]	6.77	3.47	9.9	9.9	0.077	0.005	15.7	15.6	83
13.03.96[4]	–	–	–	–	–	–	–	–	–
01.04.96[4]	1.83	0.12	10.5	10.1	0.024	0.005	17.5	16.8	144
04.06.96[4]	–	–	–	–	–	–	–	–	–
07.01.97[4]	3.98	1.32	10.0	10.0	0.051	0.005	13.5	13.4	197
08.01.97[4]	3.90	1.00	10.1	10.1	0.054	0.005	16.1	16.0	193
09.01.97[4]	3.75	0.71	10.1	10.1	0.056	0.005	14.4	14.3	199
21.01.97[4]	3.48	0.84	10.0	10.0	0.058	0.005	16.7	16.6	157
04.02.97[4]	3.82	1.26	10.5	10.5	0.072	0.029	14.7	14.6	221
17.02.97[4]	3.89	1.71	10.9	10.9	0.029	0.029	14.8	14.7	213
24.02.97[4]	–	–	–	–	–	–	–	–	–
03.03.97[4]	2.58	1.70	10.4	10.4	0.052	0.027	15.0	15.0	200
14.03.97[4]	3.47	1.41	10.8	10.8	0.079	0.028	15.5	15.4	203
26.03.97[4]	3.18	1.13	10.6	10.6	0.080	0.028	15.5	15.4	195
11.04.97[4]	3.17	1.07	10.8	10.8	0.077	0.025	16.0	15.9	204
29.04.97[4]	2.76	0.82	10.9	10.9	0.066	0.025	14.6	14.6	212
12.05.97[4]	1.58	0.52	11.3	11.3	0.045	0.026	15.4	15.4	214
26.05.97[4]	2.60	0.80	12.3	12.3	0.066	0.026	15.7	15.7	242
09.06.97[4]	2.50	0.66	11.1	11.1	0.070	0.025	14.4	14.4	215
20.06.97[4]	2.78	0.74	10.5	10.5	0.067	0.025	13.9	13.8	223
07.07.97[4]	3.34	0.91	11.5	11.5	0.095	0.032	15.3	15.2	197
22.07.97[4]	1.90	0.82	11.6	11.6	0.024	0.005	15.3	15.3	199
01.08.97[4]	3.54	1.60	11.1	11.1	0.046	0.005	14.5	14.4	173
18.08.97[4]	3.04	1.10	9.6	9.6	0.034	0.005	11.2	11.1	236
28.08.97[4]	2.89	1.22	11.6	11.6	0.033	0.005	12.5	12.5	298
19.09.97[4]	2.26	0.98	11.8	11.8	0.038	0.005	13.4	13.4	213
01.10.97[4]	1.56	0.92	11.3	11.3	0.026	0.005	13.4	13.4	231
13.10.97[4]	2.42	1.33	11.7	11.7	0.043	0.005	13.5	13.5	221
27.10.97[4]	2.38	0.84	12.0	12.0	0.049	0.012	13.6	13.6	223
11.11.97[4]	2.58	1.68	11.7	11.7	0.047	0.012	13.5	13.5	276
26.11.97[4]	2.97	2.25	11.8	11.8	0.039	0.010	13.2	13.2	275
08.12.97[4]	2.41	2.03	11.8	11.8	0.029	0.005	13.4	13.4	244
19.12.97[4]	2.83	1.99	12.1	12.1	0.034	0.005	13.1	13.1	243
20.06.00	–	–	–	–	–	–	–	–	–
21.11.00	–	–	–	–	–	–	–	–	–
07.12.00	–	0.01	12.4	12.4	–	bdl	–	13.9	207
16.01.01	12.5	0.41	11.0	11.0	bdl	bdl	12.9	12.6	200
23.01.01	–	0.90	–	13.1	–	0.001	–	12.9	–
01.02.01[5]	–	–	–	–	–	–	–	–	–
02.02.01	3.22	2.49	13.7	13.9	0.012	bdl	25.3	25.2	363
07.03.01	1.17	0.60	12.0	12.7	bdl	bdl	13.1	14.8	197
15.03.01	3.35	0.72	12.9	12.2	bdl	bdl	14.6	12.1	175
10.04.01	–	0.75	–	8.1	–	0.001	–	7.0	–
08.06.01	–	0.09	–	14.7	–	bdl	–	15.8	232
24.07.01	0.84	0.17	11.9	11.8	bdl	bdl	12.8	13.0	183
02.11.01	1.48	bdl	1.5	1.4	0.118	0.097	16.2	14.6	173
22.11.01	0.62	bdl	10.8	11.4	0.040	0.006	14.2	14.4	288
11.12.01	0.52	bdl	11.2	11.2	0.003	0.015	16.3	14.0	226
15.01.02	0.78	0.04	12.3	12.3	0.020	0.012	14.2	14.3	209
24.01.02	0.60	0.07	11.7	12.1	0.016	0.005	14.3	14.0	275

Table 6c continued

Date	Fe tot mg/L	Fe diss mg/L	Mn tot mg/L	Mn diss mg/L	Pb tot mg/L	Pb diss mg/L	Zn tot mg/L	Zn diss mg/L	Zn/Cd ratio
11.02.02	0.55	0.27	10.0	10.2	0.026	0.010	12.9	12.6	174
12.03.02	0.59	0.26	11.3	11.1	0.022	0.007	14.3	14.2	149
04.04.02	0.54	0.02	10.9	10.8	0.022	0.004	14.4	14.3	167
16.04.02	0.30	0.02	11.0	10.8	0.060	0.050	14.1	14.0	384
30.04.02	0.44	0.02	10.9	10.6	0.072	0.059	14.2	13.6	166
30.05.02	0.41	0.04	11.3	10.9	0.003	0.002	15.0	14.7	212
28.06.02	0.46	0.05	11.2	11.2	0.013	0.002	14.8	14.7	228
16.07.02	0.44	0.21	10.5	10.8	0.013	0.009	13.4	13.7	457
23.07.02	0.54	0.04	10.3	10.5	bdl	bdl	12.7	12.8	175
06.08.02	0.57	0.04	11.2	11.0	0.013	0.002	13.9	13.5	174
11.09.02	0.91	0.04	12.4	13.0	0.048	0.010	22.4	32.0	189
27.09.02	1.38	bdl	12.8	12.5	0.005	0.001	21.2	20.8	137
22.10.02	1.90	0.02	11.0	10.8	0.087	0.010	18.5	18.3	149
07.02.03	0.97	0.03	3.9	3.8	0.056	bdl	13.8	13.8	106
01.03.03	0.85	0.02	4.1	4.1	0.030	0.004	13.1	14.4	111
25.06.03	0.72	0.01	4.0	3.9	0.038	0.006	11.6	11.6	95
24.08.03	0.93	bdl	4.9	4.8	0.039	0.003	12.0	12.3	122

1 MILDE 1973, * before complete flooding
2 PETER 1983
3 HAUBRICH 2001
4 BAACKE 2000
5 WOLKERSDORFER written communication
bdl = below detection limit

were associated with the mid-depth levels, which are connected to the largest volumes of mine workings (Figure 7). In 1982, temperatures ranged from 22°C at the outfall to 37–45 °C at the shaft bottom. Conductivity values varied between 2,242 and 2,749 µS/cm (Figure 8). In 2001/2002, however, temperature (19.0-19.3 °C), electric conductivity (1,807-1,980 µS/cm) and contaminant concentrations (e.g. Zn, Cd, As, Pb, and sulfate), as well as the Zn/Cd ratio, show little depth variation, especially below 300 m.

4.4. Flow speed measurements in the Reiche Zeche shaft

High resolution flow measurements -two per depth- were made in 2001 to investigate flow rates at different depths

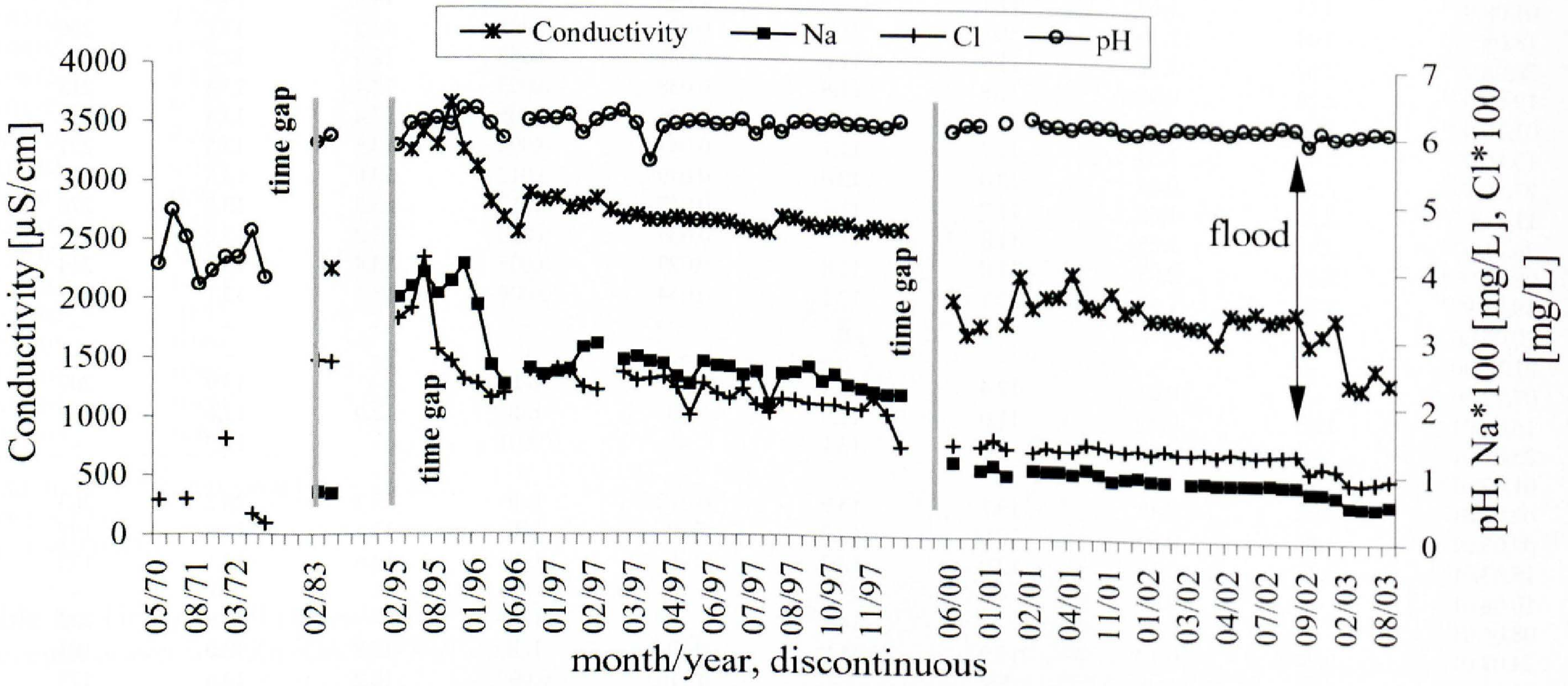


Fig. 4: Conductivity values, pH, Na, and Cl concentrations in mine water discharged at the outfall (Reiche Zeche shaft) / **Abb. 4:** Leitfähigkeit, pH-Wert sowie Na- und Cl-Konzentrationen im Grubenwasser am Überlauf (Reiche Zeche Schacht)

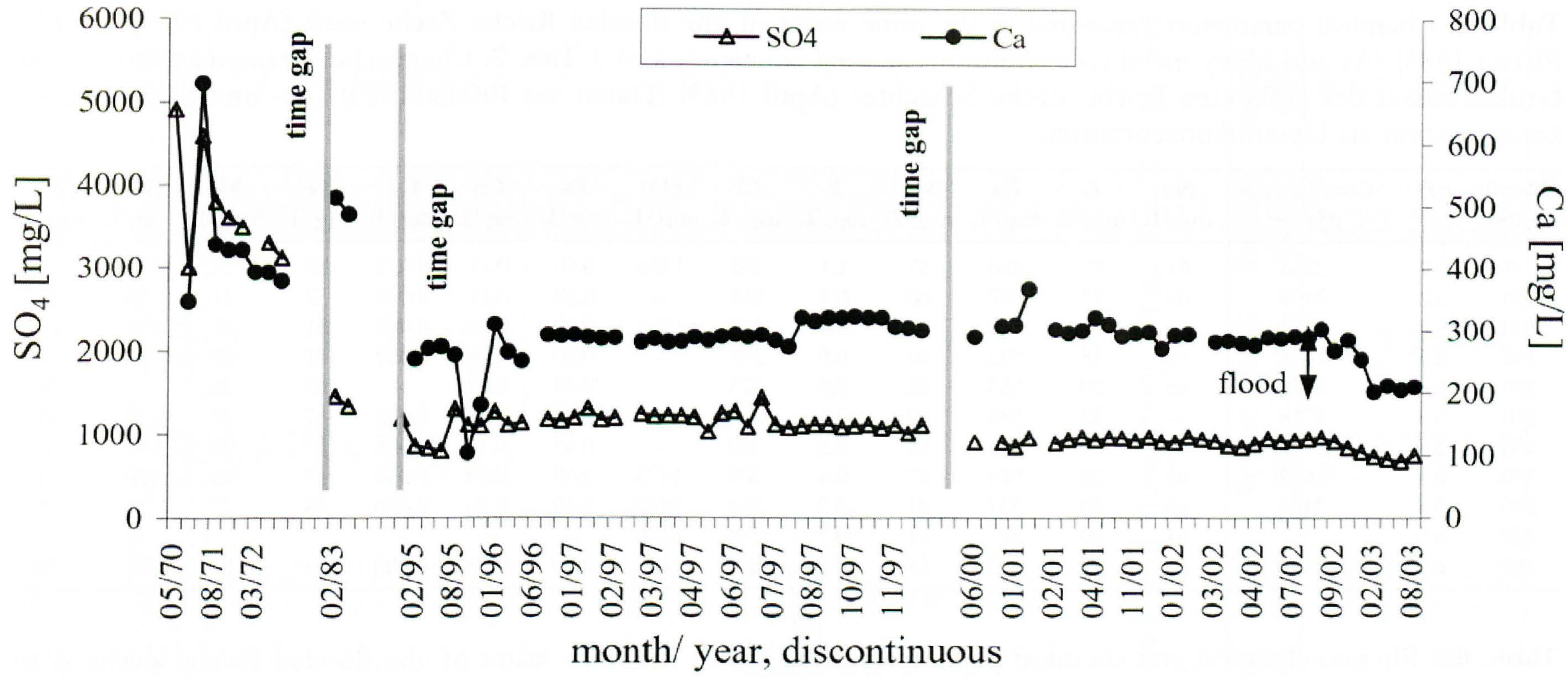


Fig. 5: Ca and SO_4 concentrations in mine water discharged at the outfall (Reiche Zeche shaft)
Abb. 5: Ca- and SO_4-Konzentrationen im Grubenwasser am Überlauf (Reiche Zeche Schacht)

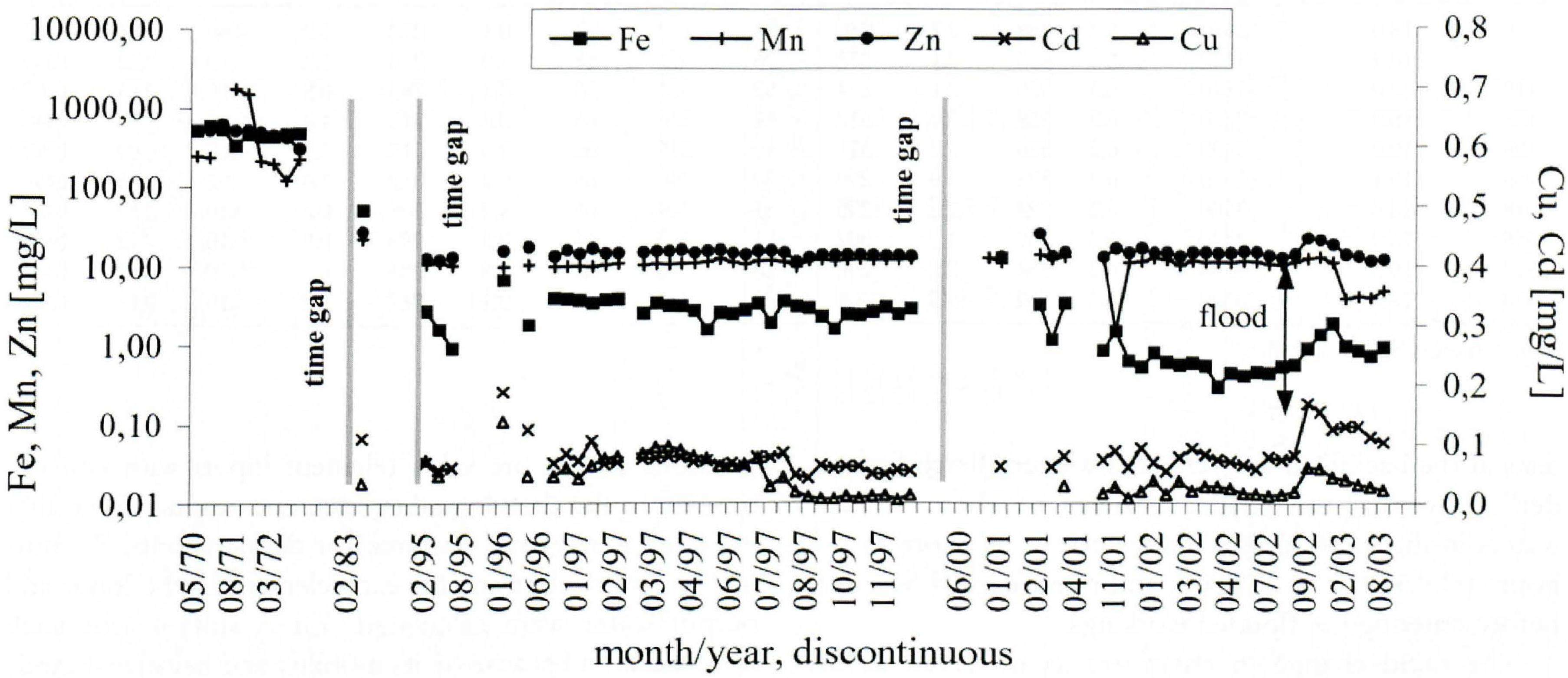


Fig. 6: Total Cd, Cu, Fe, Mn, and Zn concentrations in mine water discharged at the outfall (Reiche Zeche shaft)
Abb. 6: Gesamtkonzentrationen von Cd-, Cu-, Fe-, Mn-, and Zn- im Grubenwasser am Überlauf (Reiche - Zeche - Schacht)

of the shaft and to estimate flow into and out of the shaft at different levels. Flow velocities were 1.4 to 2.5 m/h in the deeper section (level 15 to 8) and > 1 to 3.5 m/h in the upper shaft section (level 8 to ½5) (table 15).

5. Discussion

5.1. Mobilisation, fixation, and transport of contaminants in the unflooded workings

Mass balance calculations, detailed mineralogical studies, and tracer tests in the sampling areas point to complex mobilisation-, transport- and fixation processes. Tracer

Table 7: Chemical parameters measured in the mine water of the flooded Reiche Zeche shaft (April 1983) (data by PETER 1983) (As and heavy metal concentrations as total concentration) / **Tab. 7:** Chemische Parameter gemessen im Grubenwasser des gefluteten Reiche Zeche Schachtes (April 1983) (Daten aus PETER 1983) (As- und Schwermetallkonzentration als Gesamtkonzentration)

Depth mbo	pH	Conductivity µS/cm	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	F mg/L	Cl mg/L	SO_4 mg/L	As mg/L	Cd mg/L	Cu mg/L	Fe mg/L	Mn mg/L	Pb mg/L	Zn mg/L
0	5.9	2246	61	17	486	57	1.1	255	1336	0.60	0.11	0.035	52	22	15	27
50	5.8	2499	63	17	507	60	0.7	268	–	0.58	0.11	0.045	52	21	10	28
100	5.8	2242	61	18	496	60	0.6	260	1313	0.30	0.12	0.085	51	21	10	27
140	5.8	2431	65	18	502	60	0.9	248	–	0.50	0.14	0.030	51	20	10	28
180	6.0	2669	68	20	553	62	0.9	275	–	0.44	0.22	–	65	26	–	29
240	5.8	2718	–	22	589	69	0.6	293	–	0.60	0.34	0.035	57	27	15	34
300	5.8	2749	69	22	574	66	0.5	320	–	0.45	0.34	0.035	57	28	15	33
350	5.7	2502	65	22	584	67	0.4	288	1473	1.65	0.30	0.030	57	29	20	34
380	5.8	2424	65	20	533	61	0.3	288	1422	2.10	0.20	0.050	58	27	40	29
420	6.0	–	61	20	527	61	0.7	278	1376	–	–	–	–	–	–	–
460	6.0	2484	69	22	553	64	0.3	358	1437	2.00	0.23	0.080	54	27	25	30

Table 8a: Physico-chemical and chemical parameters measured in the mine water of the flooded Reiche Zeche shaft (January 1997) (data by BAACKE 2000) / **Tab. 8a:** Physiko-chemische und chemische Parameter gemessen im Grubenwasser des gefluteten Reiche-Zeche-Schachtes (Januar 1997) (Daten aus BAACKE 2000)

Depth mbo	Temperature °C	Conductivity µS/cm	pH	Eh mV	O_2 mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	F mg/L	Cl mg/L	Br mg/L	NO_3 mg/L	HCO_3 mg/L	SO_4 mg/L
0	18.0	2830	6.2	355	2.2	236	16	290	57	0.1	232	1.2	4.80	103	1164
78	18.2	3120	6.3	355	2.1	273	26	321	58	2.0	268	1.2	0.10	122	1309
118	18.0	3140	6.3	320	2.1	294	52	321	58	0.1	283	0.8	0.10	113	1262
158	18.9	3340	6.2	328	2.2	312	41	346	65	0.6	315	1.4	0.10	98	1446
198	19.0	3400	6.2	326	2.2	311	40	346	66	2.6	315	1.3	0.10	99	1392
258	19.1	3340	6.2	325	1.9	299	34	346	66	0.4	312	1.6	1.92	105	1449
318	18.5	3400	6.2	323	2.2	295	31	349	65	4.2	308	0.8	0.10	112	1429
358	18.9	3340	6.2	339	1.7	302	21	347	66	2.6	298	0.8	0.10	112	1422
398	19.3	3300	6.2	354	2.0	296	20	346	64	2.8	285	0.1	0.10	113	1364
438	18.8	3320	6.3	363	1.9	301	20	345	62	0.1	287	1.2	0.10	117	1324

mbo = meters below outfall

tests at the backfilled ore vein "Schwarzer Hirsch Stehender" show that the residence times of these seepage waters in the unflooded workings can be as short as 1–2 hours (HAUBRICH et al. 2000) and rarely exceed 5–7 days before entering the flooded workings.

The rapid change in chemistry as observed at the backfilled ore vein "Schwarzer Hirsch Stehender" (Figure 3, Table 4) cannot be explained simply by the effects of sulfide oxidation processes during seepage, as sulfide oxidation is a relatively slow process. The addition of small amounts of old, very highly mineralised pore water from fractures and pores in the weathered vein ore material into the passing seepage water (due to capillary suction) was found to be responsible. These pore waters, with a mineralisation as high as 200 g/L and very long residence times, seem to be in quasi-equilibrium with their geochemical environment. They have formed over centuries in the highly oxidic, low pH environment of the unflooded workings (BAACKE 2000).

Mass balance calculations comparing amongst others heavy metal, As, and Al concentrations in the pore solutions of the ore veins (element input) with concentrations in the draining adits (element output) show that the mine is not only a source for contaminants. Zn-normalised concentrations for each element in the input and output water were calculated. Zn is suitable for such normalisation because of its mobility and because it rarely precipitates in the mine water environment. A balance factor was calculated by dividing the normalised input concentration (average pore water, BAACKE 2000, KOLITSCH & JUNGHANS unpublished data) by the normalised output concentration (adit water) for each element. These calculations show that after mobilisation, about 97 % of As, 93 % of Fe, 64 % of Cu and 57 % of Al remain in the mine if the pH reaches 5.5 (BAACKE 2000, KOLITSCH & JUNGHANS unpublished data). Three mechanisms are thought responsible for this effect:

- in-situ precipitation of heavy metals, Al, and As in the weathered material of the ore vein as secondary minerals, such as jarosite, scorodite, aluminite, anglesite, illite, and gypsum;

Table 8b: Al, As and heavy metal concentrations measured in the mine water of the flooded Reiche Zeche shaft (January 1997) (data by BAACKE 2000)
Tab. 8b: Al-, As- und Schwermetallkonzentrationen gemessen im Grubenwasser des gefluteten Reiche-Zeche-Schachtes (Januar 1997) (Daten aus BAACKE 2000)

Depth mbo	Al tot mg/L	Al diss mg/L	As tot mg/L	As diss mg/L	Cd tot mg/L	Cd diss mg/L	Cu tot mg/L	Cu diss mg/L	Fe tot mg/L	Fe diss mg/L	Mn tot mg/L	Mn diss mg/L	Pb tot mg/L	Pb diss mg/L	Zn tot mg/L	Zn diss mg/L	Zn/Cd ratio
0	0.50	0.97	0.078	0.003	0.084	0.083	0.017	0.044	3.9	1.0	13.0	10.1	0.049	0.005	16.1	16.0	193
78	1.30	0.21	0.110	0.002	0.064	0.063	0.008	0.018	3.8	0.43	36.0	10.3	0.036	0.005	11.3	11.2	178
118	0.47	0.15	0.370	0.007	0.064	0.063	0.016	0.014	9.3	1.2	26.0	10.1	0.120	0.005	10.7	10.5	167
158	0.11	0.14	0.120	0.003	0.082	0.081	0.005	0.011	3.1	0.92	14.0	11.5	0.018	0.005	13.6	13.5	167
198	0.07	0.10	0.120	0.008	0.087	0.086	0.004	0.010	2.8	0.73	12.0	11.4	0.012	0.005	13.9	13.8	160
258	0.14	0.17	0.180	0.015	0.086	0.085	0.011	0.010	4.9	1.3	15.0	11.2	0.053	0.005	13.6	13.5	159
318	0.06	0.17	0.110	0.031	0.084	0.083	0.004	0.010	1.9	0.01	11.0	11.7	0.017	0.005	13.4	13.3	160
358	0.07	0.14	0.110	0.005	0.098	0.094	0.007	0.012	3.2	0.68	11.0	10.9	0.015	0.005	14.0	13.9	148
398	0.14	0.17	0.130	0.002	0.093	0.091	0.007	0.011	3.8	0.41	14.0	10.9	0.015	0.005	13.7	13.6	149
438	0.11	0.17	0.130	0.002	0.098	0.097	0.006	0.012	3.8	0.48	16.0	10.9	0.012	0.005	14.4	14.3	147

tot = total concentration diss = dissolved concentration

Table 9a: Physico-chemical and chemical parameters measured in the mine water of the flooded Reiche Zeche shaft (June 2000) / **Tab. 9a:** Physiko-chemische und chemische Parameter gemessen im Grubenwasser des gefluteten Reiche-Zeche-Schachtes (Juni 2000)

Depth mbo	Temperature °C	Conductivity µS/cm	pH	Eh mV	O_2 mg/L	Li mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	F mg/L	Cl mg/L	NO_3 mg/L	HCO_3 mg/L	SO_4 mg/L
0	19.1	2010	6.0	582	0.2	0.097	111	12.2	289	64	3.2	137	2.6	24	904
39	18.4	2050	6.1	472	2.0	0.097	113	12.6	293	66	2.7	138	3.3	25	932
119	18.7	2040	6.1	440	3.0	0.098	116	12.3	293	68	2.9	137	2.4	24	927
159	18.5	2050	6.1	502	2.6	0.095	110	11.8	292	60	2.3	138	3.6	24	921
199	18.5	2080	6.2	512	3.0	0.103	117	13.0	289	66	2.2	143	2.5	24	946
259	18.4	2090	6.1	512	2.4	0.098	112	12.6	291	60	2.6	141	<0.01	24	944
389	18.4	2080	6.2	522	1.8	0.100	113	12.8	287	63	2.3	142	<0.01	23	921

mbo = meters below outfall

Table 9b: Al, As and heavy metal concentrations measured in the mine water of the flooded Reiche Zeche shaft (June 2000) / **Tab. 9b:** Al-, As- und Schwermetallkonzentrationen gemessen im Grubenwasser des gefluteten Reiche-Zeche-Schachtes (Juni 2000)

Depth mbo	Al tot mg/L	Al diss mg/L	As tot mg/L	As diss mg/L	Cd tot mg/L	Cd diss mg/L	Cu tot mg/L	Cu diss mg/L	Fe tot mg/L	Fe diss mg/L	Mn tot mg/L	Mn diss mg/L	Pb tot mg/L	Pb diss mg/L	Zn tot mg/L	Zn diss mg/L	Zn/Cd ratio
0	0.247	0.263	0.01	<0.01	0.079	0.080	0.019	0.016	0.49	0.09	12.6	12.6	0.022	0.007	14.5	14.6	183
39	–	0.283	0.17	<0.01	0.084	0.082	0.042	0.021	0.71	0.06	12.9	12.7	0.076	0.003	13.9	15.3	188
119	0.295	0.245	0.06	<0.01	0.077	0.076	0.027	0.021	1.8	0.27	12.7	12.9	0.026	0.003	14.4	14.6	191
159	0.223	0.230	0.04	<0.01	0.085	0.079	0.027	0.027	1.0	0.25	12.6	12.5	0.020	0.007	14.3	14.8	188
199	0.313	0.167	0.08	<0.01	0.078	0.079	0.031	0.019	1.6	0.17	13.0	13.2	0.030	0.004	14.9	14.9	189
259	0.241	0.200	0.09	<0.01	0.076	0.076	0.026	0.022	1.4	0.27	13.0	12.8	0.012	0.003	14.9	14.7	193
389	0.268	0.231	0.06	<0.01	0.085	0.082	0.027	0.024	1.2	0.12	13.3	12.7	0.013	0.003	15.6	14.9	181

tot = total concentration diss = dissolved concentration

Table 10a: Physico-chemical and chemical parameters measured in the mine water of the flooded Reiche Zeche shaft (March 2001) / **Tab. 10a:** Physiko-chemische und chemische Parameter gemessen im Grubenwasser des gefluteten Reiche-Zeche-Schachtes (März 2001)

Depth mbo	Temperature °C	Conductivity µS/cm	pH	Eh mV	O_2 mg/L	Li mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	Cl mg/L	HCO_3 mg/L	SO_4 mg/L
0	19.1	2040	6.1	426	3.9	0.092	100	12.1	295	55	135	63	941
119	18.5	2100	6.1	363	3.6	0.092	100	12.7	304	55	135	72	943
144	18.7	2060	6.2	368	2.9	0.089	100	12.3	292	55	134	72	926
159	18.6	2050	6.3	435	3.0	0.091	101	12.4	266	49	135	88*	928
189	18.5	2080	6.2	433	3.0	0.090	100	12.2	297	56	138	89*	957
209	18.7	2080	6.2	376	1.9	0.090	103	12.5	281	50	139	88*	966
249	18.5	2080	6.2	432	2.2	0.091	102	12.5	299	54	139	89*	958
279	18.5	2080	6.2	443	2.4	0.090	104	12.5	300	56	136	89*	930

mbo = meters below outfall * = analysis 24 h after sampling

Table 10b: Al, As and heavy metal concentrations measured in the mine water of the flooded Reiche Zeche shaft (March 2001) / **Tab. 10b:** Al-, As- und Schwermetallkonzentrationen gemessen im Grubenwasser des gefluteten Reiche-Zeche-Schachtes (März 2001)

Depth mbo	Al tot mg/L	Al diss mg/L	As tot mg/L	As diss mg/L	Cd tot mg/L	Cd diss mg/L	Cu tot mg/L	Cu diss mg/L	Fe tot mg/L	Fe diss mg/L	Mn tot mg/L	Mn diss mg/L	Pb tot mg/L	Pb diss mg/L	Zn tot mg/L	Zn diss mg/L	Zn/Cd ratio
0	0.311	0.444	0.033	0.004	0.061	0.075	bdl	bdl	1.2	0.60	12.0	12.7	bdl	bdl	13.1	14.8	197
119	0.320	0.246	0.057	0.011	0.062	0.061	bdl	bdl	2.1	0.85	13.5	13.1	bdl	bdl	14.4	15.0	246
144	0.215	0.202	0.062	0.010	0.068	0.060	bdl	bdl	1.7	0.83	14.3	13.5	bdl	bdl	14.3	14.7	245
159	0.286	0.285	0.056	0.010	0.062	0.061	bdl	bdl	1.4	0.81	13.3	13.5	bdl	bdl	14.3	14.5	238
189	0.180	0.182	0.065	0.023	0.062	0.067	bdl	bdl	1.3	0.89	12.4	13.2	bdl	bdl	13.6	14.4	215
209	0.213	0.272	0.081	0.011	0.067	0.062	bdl	bdl	1.4	0.86	13.7	14.0	bdl	bdl	14.0	14.4	232
249	0.152	0.146	0.143	0.084	0.064	0.050	bdl	bdl	1.9	1.5	13.6	12.9	bdl	bdl	14.1	13.5	270
279	0.159	0.155	0.159	0.085	0.047	0.055	bdl	bdl	2.0	1.7	13.4	13.4	bdl	bdl	13.9	13.7	249

tot = total concentration diss = dissolved concentration bdl = below detection limit

Table 11a: Physico-chemical and chemical parameters measured in the mine water of the flooded Reiche Zeche shaft (November 2001) / **Tab. 11a:** Physiko-chemische und chemische Parameter gemessen im Grubenwasser des gefluteten Reiche-Zeche-Schachtes (November 2001)

Depth mbo	Temperature °C	Conductivity µS/cm	pH	Eh mV	O_2 mg/L	Li mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	F mg/L	Cl mg/L	HCO_3 mg/L	SO_4 mg/L
0	18.9	2090	6.1	445	0.2	0.103	87.5	12.0	295	54	1.9	134	75	928
78	17.3	2100	6.4	390	–	0.102	88.9	11.9	305	57	1.8	136	73	934
119	17.3	2100	6.3	402	–	0.101	89.6	11.8	294	56	1.5	135	74	930
159	17.6	2060	6.3	421	–	0.100	86.7	11.8	297	56	1.5	132	78	892
199	16.9	2140	6.4	498	–	0.099	90.1	11.8	305	58	1.5	138	75	928
259	17.1	2130	6.4	404	–	0.099	90.0	12.1	298	57	1.6	141	75	925
318	18.0	2140	6.2	473	–	0.098	88.5	12.0	308	55	1.4	138	76	887
362	17.6	2140	6.3	462	–	0.097	90.7	12.2	310	58	1.4	138	76	880
384	17.8	2150	6.3	487	–	0.098	89.2	12.2	295	55	1.5	138	76	874

mbo = meters below outfall

Table 11b: Al, As and heavy metal concentrations measured in the mine water of the flooded Reiche Zeche shaft (November 2001) / **Tab. 11b:** Al-, As- und Schwermetallkonzentrationen gemessen im Grubenwasser des gefluteten Reiche-Zeche-Schachtes (November 2001)

Depth mbo	Al tot mg/L	Al diss mg/L	As tot mg/L	As diss mg/L	Cd tot mg/L	Cd diss mg/L	Cu tot mg/L	Cu diss mg/L	Fe tot mg/L	Fe diss mg/L	Fe^{2+} mg/L	Mn tot mg/L	Mn diss mg/L	Pb tot mg/L	Pb diss mg/L	Zn tot mg/L	Zn diss mg/L	Zn/Cd ratio
0	0.554	0.373	0.041	bdl	0.087	0.084	0.028	0.032	1.5	bdl	<0.02	14.7	14.0	0.021	0.097	16.2	14.6	173
78	0.411	0.225	0.283	bdl	0.076	0.076	0.065	0.037	13.8	0.14	0.02	13.4	14.1	0.075	0.034	13.7	14.4	190
119	0.435	0.301	0.119	bdl	0.082	0.078	0.041	0.029	5.7	0.25	0.08	14.5	14.2	0.042	0.014	15.3	14.8	190
159	0.262	0.212	0.067	bdl	0.073	0.072	0.018	0.013	2.6	0.08	0.04	13.6	13.8	0.033	0.010	14.0	13.9	192
199	0.300	0.236	0.057	bdl	0.060	0.079	0.010	0.011	1.6	0.21	0.11	13.6	14.0	0.013	0.009	13.1	14.3	180
259	0.251	0.209	0.129	0.012	0.061	0.062	0.010	0.007	2.1	0.81	0.40	14.0	14.4	0.008	0.005	13.6	13.5	219
318	0.303	0.236	0.084	bdl	0.066	0.066	0.013	0.008	1.9	0.16	0.09	13.5	14.3	0.013	0.005	13.3	14.0	213
362	0.278	0.267	0.099	bdl	0.065	0.065	0.012	0.011	2.0	0.19	0.09	13.9	13.7	0.010	0.005	13.7	13.3	204
384	0.384	0.258	0.130	bdl	0.068	0.064	0.015	0.008	4.6	0.21	0.10	13.9	13.8	0.027	0.004	13.8	13.7	215

tot = total concentration diss = dissolved concentration

Table 12a: Physico-chemical and chemical parameters measured in the mine water of the flooded Reiche Zeche shaft (January 2002) / **Tab. 12a:** Physiko-chemische und chemische Parameter gemessen im Grubenwasser des gefluteten Reiche-Zeche-Schachtes (Januar 2002)

Depth mbo	Temperature °C	Conductivity µS/cm	pH	Eh mV	O_2 mg/L	Li mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	F mg/L	Cl mg/L	HCO_3 mg/L	SO_4 mg/L
0	19.1	1869	6.0	460	0.4	0.101	87.7	11.7	294	50	1.6	133	51	973
78	17.0	1918	6.2	507	3.7	0.101	86.2	11.7	286	50	1.7	130	52	989
119	17.5	1925	6.1	507	3.8	0.099	84.4	11.9	290	57	1.8	127	46	1000
159	17.3	1954	6.2	495	3.5	0.100	86.6	11.7	294	55	2.1	131	53	988
199	17.3	1962	6.2	484	3.7	0.100	86.7	11.5	300	56	1.6	130	59	995
269	17.0	1981	6.2	446	3.8	0.101	86.1	11.8	299	55	1.8	132	65	1000
319	17.1	1977	6.3	522	3.8	0.102	85.9	11.7	282	53	1.7	133	68	989
365	17.8	1986	6.2	514	3.0	0.101	88.6	11.8	291	55	1.6	132	69	977
393	17.3	1997	6.3	526	3.9	0.102	88.5	11.4	286	51	1.4	134	72	978

mbo = meters below outfall bdl = below detection limit

Table 12b: Al, As and heavy metal concentrations measured in the mine water of the flooded Reiche Zeche shaft (January 2002) / **Tab. 12b:** Al-, As- und Schwermetallkonzentrationen gemessen im Grubenwasser des gefluteten Reiche-Zeche-Schachtes (Januar 2002)

Depth mbo	Al tot mg/L	Al diss mg/L	As tot mg/L	As diss mg/L	Cd tot mg/L	Cd diss mg/L	Cu tot mg/L	Cu diss mg/L	Fe tot mg/L	Fe diss mg/L	Mn tot mg/L	Mn diss mg/L	Pb tot mg/L	Pb diss mg/L	Zn tot mg/L	Zn diss mg/L	Zn/Cd ratio
0	0.342	0.273	0.023	bdl	0.053	0.051	0.015	0.012	0.60	0.07	11.7	12.1	0.016	0.005	14.3	14.0	275
78	1.080	0.801	0.071	bdl	0.075	0.070	0.049	0.035	3.10	0.10	13.3	12.7	0.031	0.005	17.0	16.5	237
119	1.730	1.140	0.277	bdl	0.095	0.085	0.082	0.056	10.6	0.22	12.8	12.8	0.087	0.013	19.8	19.2	226
159	1.050	0.706	0.113	bdl	0.072	0.067	0.047	0.031	4.2	0.14	12.8	12.4	0.057	0.006	16.6	16.0	237
199	1.350	0.878	0.104	bdl	0.073	0.070	0.056	0.040	4.4	0.14	12.6	12.8	0.059	0.003	16.9	17.2	246
269	0.724	0.573	0.111	bdl	0.065	0.059	0.035	0.023	2.7	0.46	12.4	12.5	0.030	0.006	15.1	15.2	259
319	0.878	0.526	0.178	bdl	0.070	0.063	0.035	0.022	3.7	0.09	12.7	12.2	0.072	0.003	15.8	15.1	241
365	0.654	0.522	0.073	bdl	0.065	0.061	0.036	0.022	0.04	0.08	12.4	12.6	0.024	0.003	15.4	15.4	251
393	0.713	0.554	0.095	bdl	0.065	0.062	0.031	0.021	0.03	0.02	11.5	12.3	0.037	0.006	14.2	15.1	242

tot = total concentration diss = dissolved concentration

Table 13a: Physico-chemical and chemical parameters measured in the mine water of the flooded Reiche Zeche shaft (April 2002) / **Tab. 13a:** Physiko-chemische und chemische Parameter gemessen im Grubenwasser des gefluteten Reiche-Zeche-Schachtes (April 2002)

Depth mbo	Temperature °C	Conductivity µS/cm	pH	Eh mV	O_2 mg/L	Li mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	F mg/L	Cl mg/L	NO_3 mg/L	HCO_3 mg/L	SO_4 mg/L
0	19.0	1807	6.1	472	0.3	0.094	87.0	12.3	283	52.5	1.9	129	3.7	78	862
81	18.3	1883	6.3	557	4.0	0.095	87.8	12.3	285	52.1	2.0	124	2.0	72	872
122	18.2	1888	6.2	536	3.8	0.096	86.3	11.9	278	51.2	1.8	125	1.6	95	883
163	18.4	1936	6.2	563	4.0	0.091	86.0	12.1	288	52.4	1.7	132	2.1	94	892
209	18.4	1952	6.3	536	3.0	0.092	87.5	12.3	288	53.3	bdl	139	2.3	92	907
269	18.4	1968	6.3	557	2.9	0.091	88.0	12.4	286	52.6	1.1	130	bdl	85	880
317	18.1	1964	6.3	541	3.7	0.091	83.3	12.6	291	51.6	1.1	133	bdl	89	851
362	18.0	1967	6.4	548	3.9	0.091	89.0	12.8	294	53.1	bdl	140	2.7	89	865
392	18.0	1966	6.3	503	3.6	0.092	88.0	12.0	291	53.5	bdl	137	3.4	77	862

mbo = meters below outfall   bdl = below detection limit

Table 13b: Al, As and heavy metal concentrations measured in the mine water of the flooded Reiche Zeche shaft (April 2002) / **Table 13b:** Al, As and heavy metal concentrations measured in the mine water of the flooded Reiche Zeche shaft (April 2002)

Depth mbo	Al tot mg/L	Al diss mg/L	As tot mg/L	As diss mg/L	Cd tot mg/L	Cd diss mg/L	Cu tot mg/L	Cu diss mg/L	Fe tot mg/L	Fe diss mg/L	Fe^{2+} mg/L	Mn tot mg/L	Mn diss mg/L	Pb tot mg/L	Pb diss mg/L	Zn tot mg/L	Zn diss mg/L	Zn/Cd ratio
0	0.445	0.424	bdl	bdl	0.082	0.086	0.029	0.024	0.537	0.022	<0.01	10.9	10.8	0.022	0.004	14.4	14.3	167
81	0.801	0.626	bdl	bdl	0.088	0.087	0.044	0.030	1.79	0.026	0.03	11.9	11.2	0.032	0.009	16.2	15.3	177
122	2.120	0.404	2.70	bdl	0.220	0.078	0.108	0.026	3.50	0.044	–	11.5	11.2	0.829	0.002	16.1	14.9	192
163	0.780	0.536	0.31	bdl	0.098	0.080	0.045	0.026	5.80	0.048	–	11.6	11.5	0.114	0.004	15.3	15.0	187
209	0.644	0.551	0.09	bdl	0.086	0.080	0.035	0.027	1.83	0.047	0.01	11.5	11.5	0.036	0.003	15.0	15.0	187
269	0.548	0.476	0.09	bdl	0.094	0.087	0.037	0.027	1.68	0.043	0.08	11.9	11.6	0.023	0.008	15.6	15.3	176
317	0.566	0.450	0.19	bdl	0.099	0.089	0.036	0.028	2.13	0.159	0.04	12.1	11.5	0.048	0.006	16.3	15.3	171
362	0.568	0.448	0.18	bdl	0.100	0.089	0.036	0.025	2.16	0.099	0.01	11.4	11.2	0.028	0.005	15.2	14.9	168
392	0.446	0.398	0.09	bdl	0.092	0.088	0.033	0.026	1.61	0.202	0.08	11.2	11.3	0.024	0.006	14.7	14.9	169

tot = total concentration   diss = dissolved concentration

Table 14a: Physico-chemical and chemical parameters measured in the mine water of the flooded Reiche Zeche shaft (October 2002) / **Tab. 14a:** Physiko-chemische und chemische Parameter gemessen im Grubenwasser des gefluteten Reiche-Zeche-Schachtes (Oktober 2002)

Depth mbo	Temperature °C	Conductivity µS/cm	pH	Eh mV	O_2 mg/L	Li mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	F mg/L	Cl mg/L	NO_3 mg/L	HCO_3 mg/L	SO_4 mg/L
0	16.6	1890	6.0	494	5.5	0.090	69.0	11.2	253	47	1.1	108	3.5	70	788
79	17.5	1817	5.9	516	4.2	0.089	67.9	11.1	259	45	1.0	106	3.4	69	760
121	17.7	1757	6.0	509	4.6	0.087	68.8	11.4	256	47	bdl	106	4.0	63	747
161	17.6	1787	6.0	525	4.4	0.087	68.6	11.2	260	46	bdl	106	4.1	61	755
202	17.8	1700	6.0	532	3.8	0.087	67.3	11.2	252	46	1.1	105	4.0	61	741
262	17.5	1670	6.0	499	4.0	0.085	65.9	11.0	251	47	1.1	103	4.6	60	720
323	17.3	1567	6.1	511	3.7	0.084	65.6	11.2	249	46	1.2	103	5.0	61	716
367	17.5	1537	6.1	494	3.8	0.084	65.7	11.1	243	47	1.1	100	5.0	62	697

mbo = meters below outfall   bdl = below detection limit

Table 14b: Al, As and heavy metal concentrations measured in the mine water of the flooded Reiche Zeche shaft (October 2002) / **Tab. 14b:** Al-, As- und Schwermetallkonzentrationen gemessen im Grubenwasser des gefluteten Reiche-Zeche-Schachtes (Oktober 2002)

Depth mbo	Al tot mg/L	Al diss mg/L	As tot mg/L	As diss mg/L	Cd tot mg/L	Cd diss mg/L	Cu tot mg/L	Cu diss mg/L	Fe tot mg/L	Fe diss mg/L	Fe 2+ mg/L	Mn tot mg/L	Mn diss mg/L	Pb tot mg/L	Pb diss mg/L	Zn tot mg/L	Zn diss mg/L	Zn/Cd ratio
2	0.697	0.532	0.126	0.005	0.126	0.123	0.044	0.034	1.9	0.02	0.08	11.0	10.8	0.087	0.010	18.5	18.3	149
79	0.467	0.392	0.065	0.005	0.122	0.121	0.030	0.026	0.90	0.02	0.06	11.1	10.9	0.052	0.011	18.3	18.0	149
121	0.450	0.412	0.056	0.005	0.128	0.127	0.029	0.028	0.61	0.03	0.07	11.0	10.9	0.044	0.014	18.1	18.0	142
161	0.436	0.408	0.050	0.006	0.128	0.126	0.030	0.025	0.54	0.03	0.07	10.8	11.0	0.043	0.015	17.9	18.0	143
202	0.444	0.414	0.042	0.005	0.129	0.128	0.030	0.026	0.55	0.02	0.12	11.0	10.9	0.035	0.011	18.1	17.9	140
262	0.646	0.393	0.343	0.005	0.139	0.129	0.042	0.024	5.33	0.02	0.08	10.9	10.9	0.140	0.007	18.0	17.8	138
323	0.571	0.419	0.255	0.007	0.135	0.128	0.033	0.026	1.8	0.03	0.10	10.6	10.5	0.070	0.009	17.6	17.4	136
367	0.465	0.416	0.067	0.006	0.130	0.127	0.030	0.025	0.69	0.02	0.09	10.7	10.4	0.035	0.008	17.7	17.4	137

mbo = meters below outfall tot = total concentration diss = dissolved concentration

- precipitation of secondary phases, e.g. as hydroxo-complexes, with Fe, Al, Cu, As, Zn, Pb, and Mn, during mixing of acid and neutral mine water or due to buffering reactions with siliceous or carbonate minerals; and
- co-precipitation (adsorption) of heavy metals, As, and Al with armorphous Fe- and Al-hydroxides and -hydroxosulfates, ferrihydrite, schwertmannite, goethite, alumogel or (hydro-) basaluminite. The affinity of elements towards these precipitates was found to be (BAACKE 2000): As>Fe>Al>Cu>Zn, Cd>Pb, Mn. The retardation effect is low for Zn, Cd, Pb, Mn, and Ni.

5.2. Characterisation of the Mine Water at the Outfall

The initial strong decrease of deposit-related mineralisation after flooding in 1971, the increase of pH and the development of water temperature as well as the slowing down or stabilisation of parameter changes since the beginning of the 80's to mid 90's show the progressing onset of an equilibrium compared to the situation just after flooding.

However, since 1997, Zn and Cd concentrations have not changed considerably, though they are highly reflective of the influence of the pH-neutral, slightly mineralised ground water, the slightly to moderately mineralised seepage water from the unflooded mine workings, and the constant addition of small amounts of highly mineralised pore water in the flooded part of the mine. Due to the low oxygen concentrations, sulfide oxidation is very limited in the flooded part of the mine. Zn and Cd in the mine water are mainly mobilised from sphalerite (and galena) with a constant Zn/Cd ratio of about 100 (the same as in the Freiberg ore). However, between 1985 and 2002, the average Zn/Cd ratio in the water from the flooded part of the mine was 210 (Table 6c), suggesting a higher mobilisation rate for Zn. There are significant variations with time; Zn/Cd values show a standard deviation of 22% (max. 74%) from the median value, suggesting a relatively variable Zn and/or Cd source in terms of water quantity and/or concentration, since significant Cd and Zn fixation would be unusual. This is believed to be due to the mentioned inflow from the Morgenstern mine. Varying inflow rates with Zn/Cd ratios between 45 and 120 can cause the observed variations in the Zn/Cd-ratio of the Freiberg mine water.

In contrast to Zn and Cd, As and Pb show only low concentrations in solution. Their major fractions are fixed to particles, mostly to Fe-hydroxides. Hence, overall concentrations of Pb and As are proportional to the amount of particulate Fe and show a fairly good correlation with the total Fe concentrations (Figure 9).

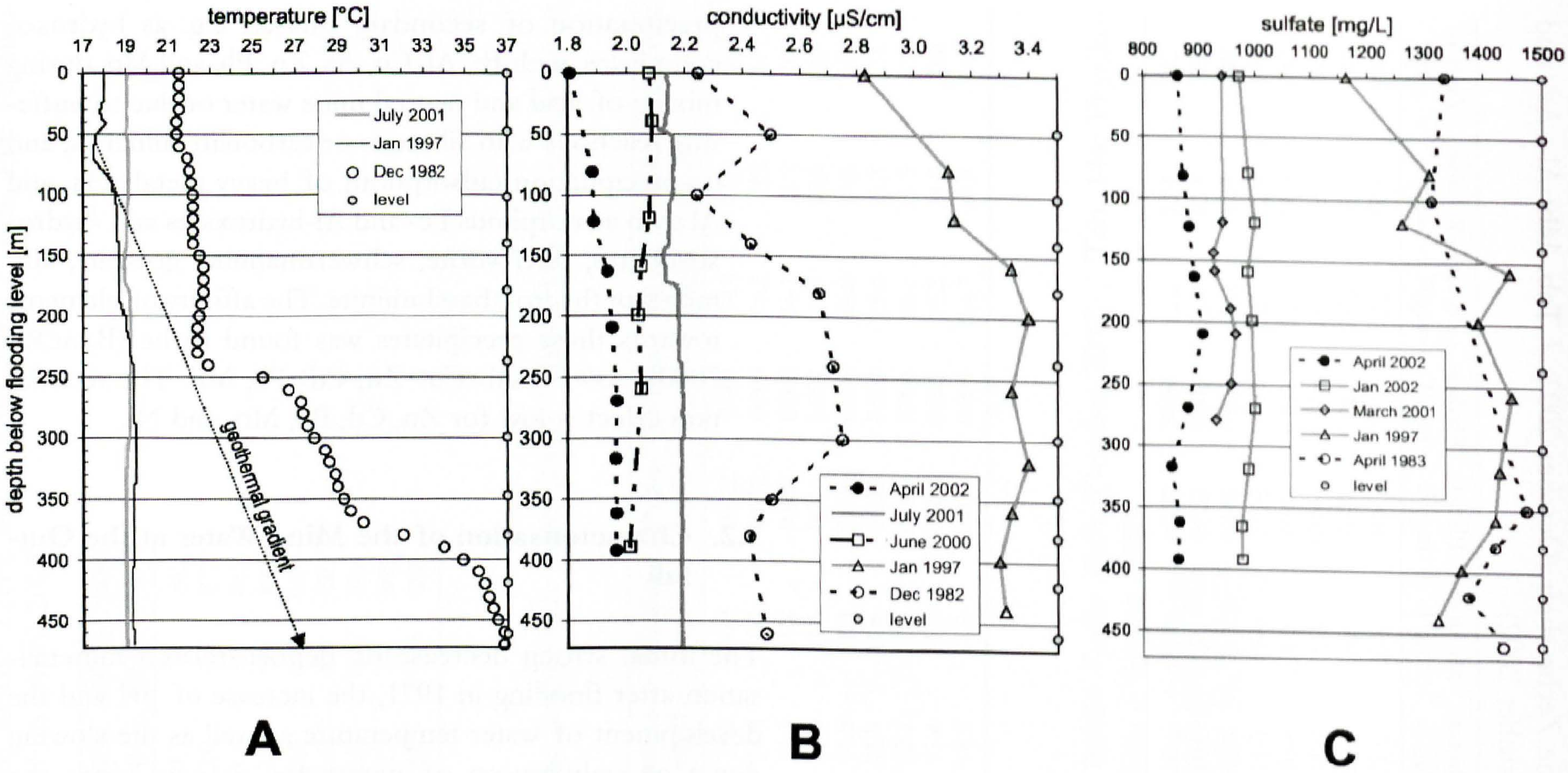


Fig. 7: Zn (A) and Cd (B) concentration and Zn/Cd ratio (C) profiles over time in the flooded Reiche Zeche shaft (data by PETER 1983, BAACKE 2000, 2000-2002 this study)
Abb. 7: Zeitabhängige Tiefenprofile der Zink- (A) und Cadmium- (B) Konzentration und des Zn/Cd-Verhältnises(C) im gefluteten Reiche-Zeche-Schacht (Daten von PETER 1983, BAACKE 2000, 2000-2002 diese Studie)

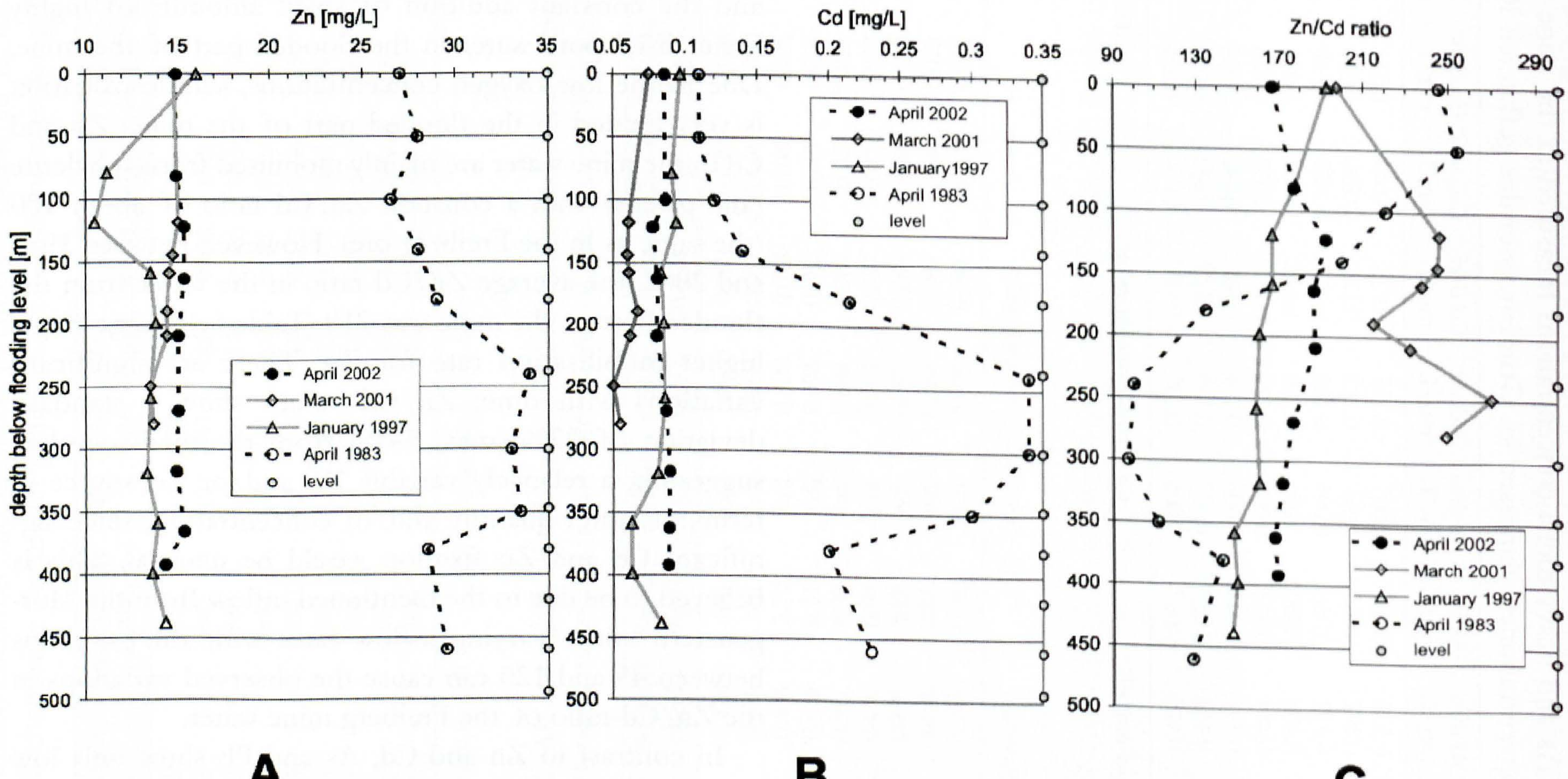


Fig. 8: Temperature (A), conductivity (B), and sulfate concentration (C) profiles over time in the flooded Reiche Zeche shaft (data by KATZWEDEL 1982, PETER 1983, BAACKE 2000, 2000-2002 this study)
Abb. 8: Zeitabhängige Temperatur- (A), Leitfähigkeits- (B), und Sulfatkonzentrationsprofile (C) im gefluteten Reiche-Zeche-Schacht (Daten aus KATZWEDEL 1982, PETER 1983, BAACKE 2000, 2000-2002 diese Studie)

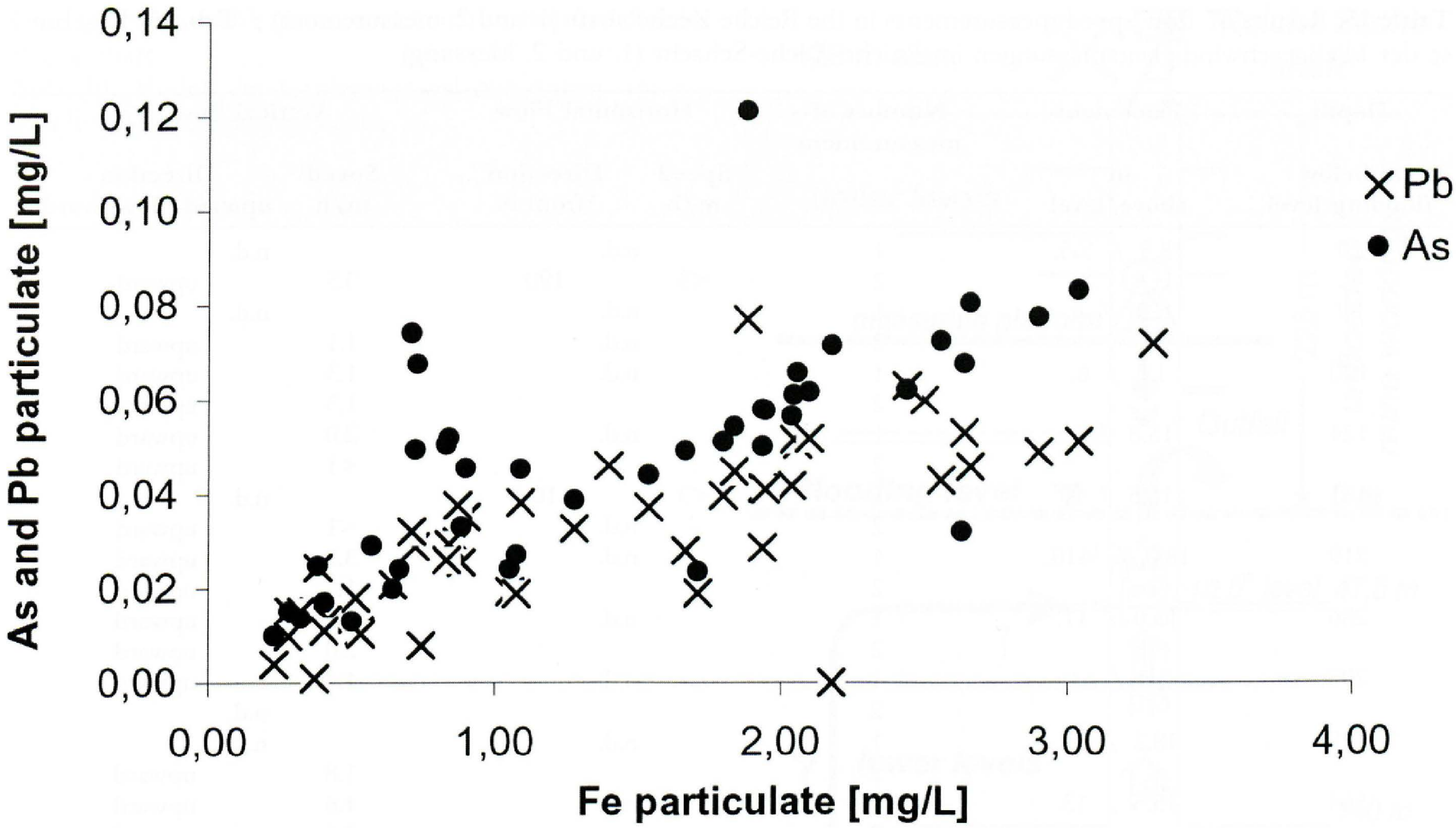


Fig. 9: Correlation between particulate As and Fe concentration and Pb and Fe concentration
Abb. 9: Korrelation zwischen partikulären As und Fe-Konzentrationen und zwischen partikulären Pb und Fe-Konzentrationen

Na, Ca, and Cl concentrations seem to be primarily controlled by the use of fertilisers and road salt (predominately NaCl, minor Na_2SO_4 and Ca-Mg-Cl (1985 only)). The mine drainage from the central Freiberg mine and the Rothschönberger Stolln adit show a Na/Cl molar ratio proportional to the dissolution of NaCl (~1). However, between 1995 and 1998, the strong variations of the equivalent concentrations of Na and Cl with a clear excess of Na over Cl (Na/Cl ~ 2.6 in 1995) cannot be explained in this manner (Figure 4). The short-term increase in the electric conductivity in that year was caused by additional Na- and sulfate input, probably due to the dewatering of tailings in the Morgenstern mining area starting in 1993. Na-rich seepage water (NaOH was used for neutralisation of acidic sludge from Zn-ore processing) was drained into the Morgenstern mine and then apparently mixed with the Freiberg mine waters. This supports the assumption of a hydraulic connection between the two mines (Figures 1 and 2). However, this process seems to have stopped since recent analysis in the Morgenstern mine indicate a clear Na depletion relative to Cl (Na/Cl~0.43). Therefore other fluctuating sources, such as the use of Na-enriched fertilisers (e.g. Na_2SO_4), might be responsible for the current observations.

5.3. Water quality development along the shaft

The fairly constant concentrations of deposit-related contaminants (e.g. Zn, Cd, Pb, As, Ca, sulfate) together with little variations in temperature (as predicted in BAACKE & DEGNER 2000), electric conductivity and pH/Eh along the profile of the Reiche Zeche shaft imply a fairly good mixing of the chemically different water types.

The depth-dependent mineralisation and contaminant concentration of the mine water observed in 1983 has significantly weakened by 1997 and ceased by 2000 (Figures 7 and 8). Consequently, since about the mid-1990s at the latest, about 25 years after flooding, it appears that the contaminant levels in the drainage of the Freiberg mine are predominantly controlled by the input from the unflooded upper part of the mine, supplying more or less constant contamination loads.

Minor changes in the physical properties and/or contaminant concentrations occur only along the upper levels of the shaft. They are the result of temporary variations in seepage water inflow (composition and/or quantity) from the unflooded part of the mine, caused by precipitation events or snow melting, as observed in Winter/Spring 2002 (Figure 8).

Table 15: Results of flow speed measurements in the Reiche Zeche shaft (1. and 2. measurement) / **Tab. 15:** Ergebnisse der Fließgeschwindigkeitsmessungen im Reiche-Zeche-Schacht (1. und 2. Messung)

Depth	Placement	Number of measurement	Horizontal Flow		Vertical flow	
m below flooding level	m above/level		Speed m/h	Direction °from N	Speed m/h	Direction upward/downward
29	18.5 / ½5.	1	n.d.		n.d.	
		2	<3	190	3.5	upward
89	12.8 / 6.	1	n.d.		n.d.	
		2	n.d.		1.1	upward
100	1.8 / 6.	1	n.d.		1.3	upward
		2			1.3	upward
124	15.8 / 7.	1	n.d.		2.0	upward
		2			<1	upward
161	16.5 / 8.	1	<3	10	n.d.	
		2	n.d.		<1	upward
219	18.0 / ½10.	1	n.d.		3.2	upward
		2			1.8	upward
286	13.0 / 11.	1	n.d.		2.0	upward
		2			2.0	upward
297	2.0 / 11.	1	n.d.		1.4	upward
		2			n.d.	
329	18.2 / 12.	1	n.d.		n.d.	
		2			1.8	upward
364	15.5 / 13.	1	n.d.		1.6	upward
		2			2.0	upward
449	12.0 / 15.	1	n.d.		n.d.	

n.d.=notdetected

5.4. Hydraulics in the flooded mine workings

The flow and flow direction speed measurements supplied information about the character and depth of a possible circulation system in the flooded mine. A clear upwards current was measured from below the 13th level up the complete shaft to the outfall (Figure 10). However, constant temperatures and electric conductivities between the 13th and 15th level (Figure 7) prove that water was also flowing in the deepest part of the shaft.

Frequent changes between laminar and turbulent flow were observed at all depths. Lateral flow could be determined at the 8th and the ½5th levels. Combined with observed flow speed reductions and increases respectively at these levels, this could indicate a discharge (8th level) from and in-flow (½5th level) into the shaft (Figure 10). The dominant driving forces for this back-flow are thought to be temperature and/or density but could not be specified.

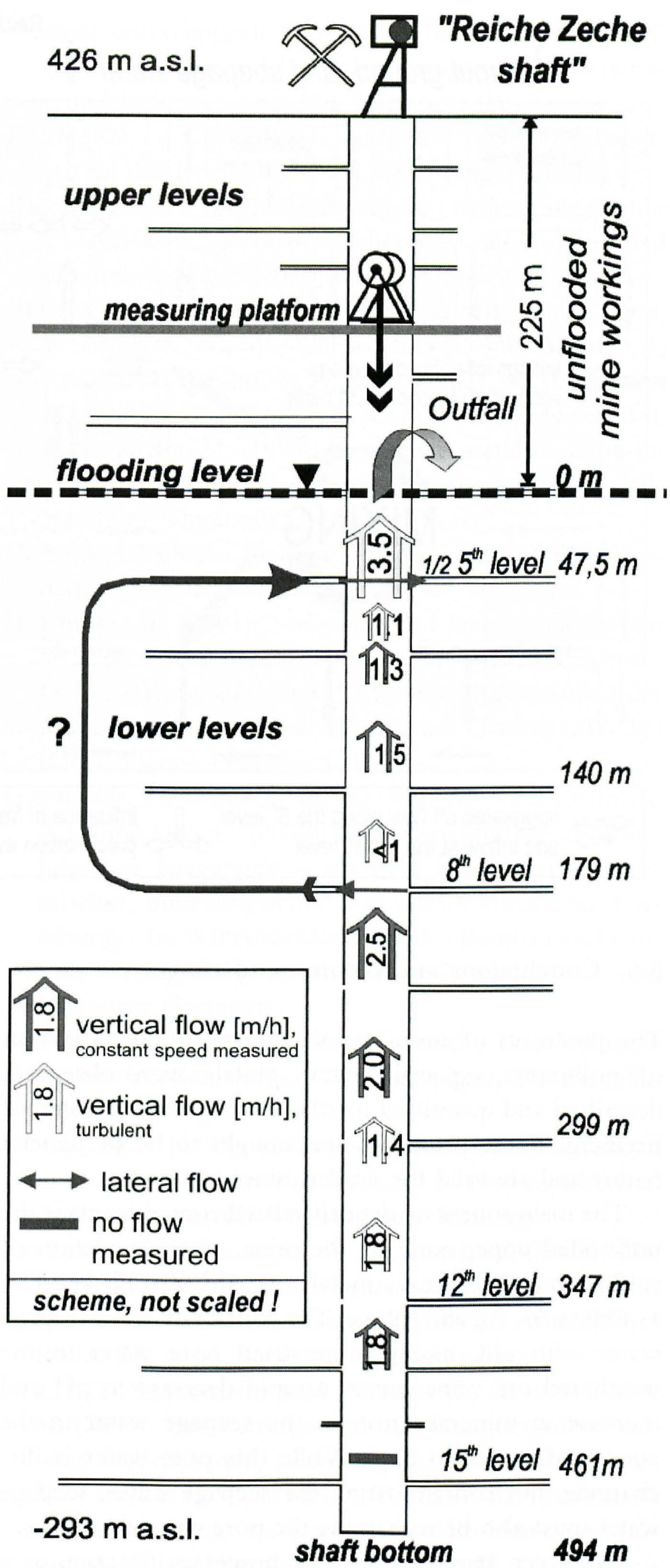
Today, we find constant temperature and electric conductivity, only minor changes in chemical concentrations and a definite upwards flow at all depths in the entire shaft. This again suggests a good mixing of the chemically very different seepage and ground water before the water enters the Reiche Zeche shaft. At all major levels, inflow or outflow with maxima at mid-level (8) and higher (½ 5) levels can be assumed (Figure 11). However, the validity of flow speed and direction measurements will have to be confirmed by additional tests.

5.5. Complex interpretation

After the initial flushing of highly mineralised waters of the oxidation zone in the years after the flooding, concentrations of deposit-related contaminants (e.g. Zn, Cd, Pb, As, Ca, sulfate) decreased continuously and pH rose. An equilibrium in the hydraulic conditions, expressed by constant contaminant concentrations was formed, which can easily be disturbed by external influences. This system can be described as follows.

After reaching the flooded workings, seepage and ground water warm up and mix while sinking down to deeper parts of the mine. One or more hydraulic head, temperature and density driven circulation or convection systems continuously exchange the deeper, warmer water with the upper, colder water. A higher mineralised inflow with high sulfate, Ca, Mg, and Na concentrations and medium Zn and Cd concentrations (to fit the element balance discussed above) from the Morgenstern Mine is being added to the system along one of the upper levels. Wall rock temperatures must have decreased considerably

Fig. 10: Mine water flow model in the flooded Reiche Zeche shaft
Abb. 10: Modell der Grubenwasserbewegungen im gefluteten Reiche-Zeche-Schacht



over the past decades, leaving only a weakened local geothermal gradient, now estimated at 1.3 °C/100 m (compared to 3.2 °C/100 m in the Freiberg area). Continuous recharge of seepage and ground water leads to an influx at all levels of about 4m^3/min of well-mixed mine water into the Reiche Zeche shaft, where the mine water rises to the outfall, and drains into the Rothschönberger Stolln.

During precipitation events and periods of intensive snow melting, shortcuts between the fresh seepage water input and the rising water in the Reiche Zeche shaft can be established temporarily along one of the upper levels (Figures 10 and 11). This can cause temporary changes in water properties (e.g. Cd in Figure 7) as well as a changing influx of seepage water from the Morgenstern mine.

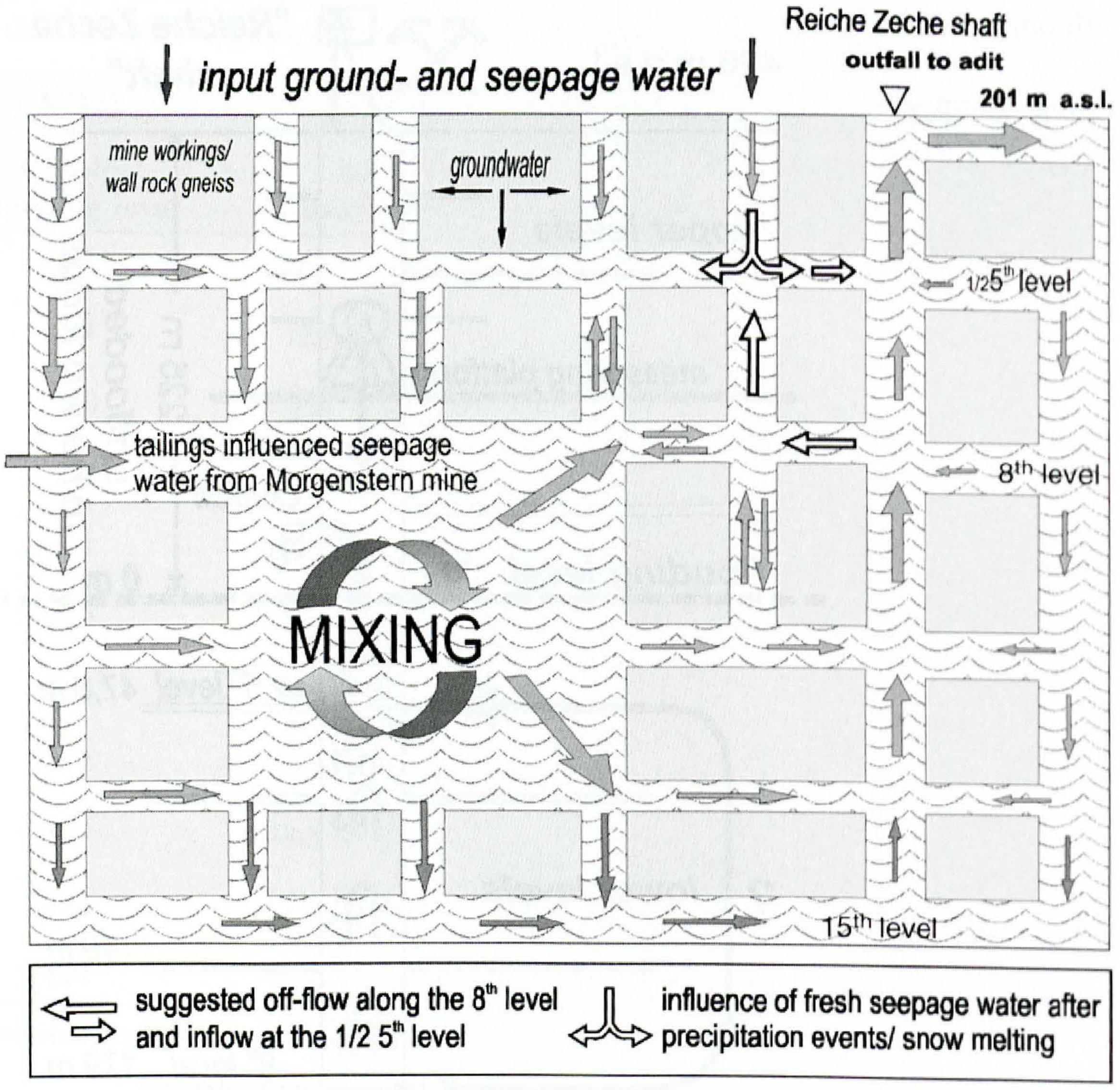


Fig. 11: Hydraulics in the flooded mine workings of the central Freiberg mine: flow scheme
Abb. 11: Hydraulische Verhältnisse im gefluteten Grubenbereich der Freiberger Grube: Fliessschema

5.6. Conclusions and recommendations

The processes of mobilisation, transport and re-fixation of pollutants, especially heavy metals, were observed, described and quantified for the former vein ore mine of Freiberg. These processes are thought to be of general nature and are valid for similar mines.

The main source of deposit-related contaminants is the unflooded upper zone of the mine, where oxidation of sulfides mobilises heavy metals (e.g. Cd, Zn, Pb and Cu) as well as As, Al, and sulfate. The contact of fresh seepage water with old, highly mineralised pore water in the weathered ore veins causes a rapid decrease in pH and increase in mineralisation in the seepage water in the course of hours to days. While this pore water is discharging and contaminating the seepage water, seepage water must also be recharging the pore water reservoirs.

However, parallel buffering processes function as a natural barrier system. Increased pH leads to precipitation and adsorption/co-precipitation of heavy metals, As, and Al. Thus, the mine acts as both a source and a sink for contaminants. After mobilisation, precipitation and co-precipitation processes about 97 % of As, 93 % of Fe, 64 % of Cu, and 57 % of Al are removed from the water while it is still in the mine. These processes occur in both the unsaturated and the saturated (flooded) zones. However, the quantitative fraction of contaminant removal for each compartment is still uncertain.

The formation of one or more circulation or convective systems is suggested. Today, physical and chemical properties of the discharging mine water are relatively constant in depth and time, suggesting good mixing and homogenisation of the chemically different ground and seepage water input. Even precipitation events or snow melting periods only affect the upper levels. A combination of water balance, chemical and isotopic data suggest the influence of tailings-influenced seepage water from the neighbouring Morgenstern Mine.

At the outfall, the water quality over the last 10 years has been relatively stable, in contrast to significant improvement for the preceding 20 years, following the inundation of most of the mine in 1971. It appears that significant heavy metal concentrations can be expected for at least several decades. The mine water from the central Freiberg deposit was and remains one of the major sources of heavy metals and As in the Mulde and Elbe rivers.

Prevention of the enormous contaminant output requires that the seepage water in the unflooded part of the mine is captured and diverted using drains before it becomes contaminated. This would reduce the recharge of pore water and limit the reaction and exchange processes between pore and seepage water, and, hence, lower contaminant loading. Alternatively, heavy metals could be fixed by artificially induced precipitation in the flooded mine workings themselves, in underground reaction areas (ponds, etc.), or in the major adits. This would require the addition of some high pH water, a reactive substance (e.g. lime) or the construction of some sort of geochemical barrier. Generally, a long lasting output of high contaminant concentrations can be prevented best by a maximum flooding to reduce the most reactive oxygen saturated zone to a minimum. This measure, however, would lead to a number of grave impacts on the environment, which would have to be considered carefully.

Data from hydrochemical monitoring in polymetallic ore mines from the beginning of the overflow after the flooding over a time span of more than 30 years are scarce. However, these data are imperative in order to improve the forecast of the temporal development of As and heavy metal concentrations in mine waters and provide an outlook about the long-term pollution of surface waters. The available longterm data series in combination with the favourable conditions in the Freiberg mine support the continuation of the monitoring program after the installation of a permanent monitoring station.

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