# Hydrochemical and isotopegeochemical evaluation of density stratification in mine water bodies of the Ruhr coalfield

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**Abstract** After mining activities in the Ruhr coalfield ceased, mine water rises in the mine excavations. In flooded shafts distinct stratification patterns between differently mineralised and stagnant water bodies have been observed at a variety of locations. The influx of more brine-type water from the surrounding rock mass and the mine workings on the one hand and the infiltration of less mineralised meteoric waters on the other hand causes substantial density differences in the mine water column. Temporal stability of stratification was proven by continuous, depth-based geophysical measurements in combination with hydrochemical and isotope geochemical investigations on levelled samples.

**Key words** IMWA 2017, stable isotopes, stratification, hard coal mining, Ruhr coalfield

## Introduction

By the end of 2018, the last remaining active coal mine in Germany's largest hard-coal mining area, the Ruhr District, will be closed. The phase of post-mining will be taking over active mining operations with its major aim to manage the complex tasks around mine closures. Risk assessment and monitoring is a key perspective of the research associated with post-mining and will be conducted in close collaboration with the mining authorities and companies. With a maximum population density of 2,800 people per km², the Ruhr District is the largest urban agglomeration in Germany and one of the most densely populated coal mining areas worldwide. Early coal mining activities date back to the 12$^{th}$ century. Since then, a total of about 10 billion tonnes of coal has been produced (Melchers 2015a). As the coal-bearing Upper Carboniferous strata is gently dipping to the north the extensive underground mining process reached a maximum depth of 1,500 m below the surface in the northern part of the mined Ruhr coal deposit. As a consequence, numerous shafts and boreholes were drilled to enable mining of deep coal seams during the active production phase. Some of these shafts were used to install submersible pumps for mine water drainage in order to retain the groundwater at a certain level. Currently, there are 11 mine water management facilities which are pumping more than 60 million m³ water per year (GVST 2015). Moreover, the existing drainage system must be maintained for the future to prevent urban and rural areas from being flooded or impacted by mine water due to subsidence associated with the extensive mining operations. Therefore, adjusted water management measures will continue in perpetuity after coal mining has ceased. Within the decommissioning area abandoned mine shafts are filled with water to varying degrees and hence provide an excellent possibility to monitor the water quality trend with depth. Depending on the geology and tectonics of the surrounding strata and the shaft lining mine cavities are pathways for heat and material flows between the ground-water reservoir, other geological strata and the atmosphere. Monitoring measures reveal stratification of mine water bodies at some of the investigated sites. Those are characterised by substantial changes in electrical conductivity (EC) as a measure of electrolyte (dissolved ionisable constituents) inventory/total dissolved solids (TDS) and/or temperature both affecting density as a major controlling factor to separate off homogenous bodies of water. Individual water bodies typically have constant levels of temperature, EC, and hence, density throughout the water column and can be regarded as "fully mixed" or equilibrated. Geophysical measurements and depth-differentiated sampling in flooded abandoned mine shafts, monitoring wells and boreholes located in the Ruhr District are carried out as part of on-going investigations to evaluate stratification patterns in mine water bodies. Understanding the development of the chemical composition and possible density layering of rising mine water in disused collieries plays a key role in any risk assessment process affecting environmental impact. In the following contribution one site that has been investigated throughout this study is presented as an example.

## Methods

Down-hole measurements are conducted using a multi-parameter probe which not only measures pressure, temperature and EC of the fluid but also pH, reduction-oxidation (i.e. redox potential) and dissolved oxygen. With a diameter of up to 45 mm, a length of 1.5 m and a system of measurement cables up to 1.000 m in length the probe records a continuous profile of the borehole fluid properties with depth. The probe's specifications are presented in Table 1.

***Table 1** Technical specifications of the used multi-parameter probe*

| Parameter | Range | Accuracy | Resolution |
|---|---|---|---|
| Pressure | 0..1000 dbar | 0.05 % F.S. | 0.0015 % F.S. |
| Temperature | 1..+50 °C | 0.005 °C | 0.001 °C |
| EC | | | |
| *Salt water* | 0..70 mS/cm | 0.007 mS/cm | 1.1 mS/cm |
| *Fresh water* | 0..7000 µS/cm | 5 µS/cm | 0.1 µS/cm |
| Oxygen | 0..50 ppm | 1.1 ppm | 1.1 ppm |
| pH | 0..14 pH | 0.01 pH | 0.001 pH |
| Redox | +/- 1000 mV | 1 mV | 0.1 mV |

Since the conductivity in an electrolyte solution is essentially dependent on the concentration of electrolytes, the measured EC is a useful indicator of TDS. The results are commonly used to determine the mixing of fresh/meteoric and saline water, i.e. brine. In order to obtain comparable results, the measured values must be referenced to a uniform reference temperature, because EC is dependent on temperature (Langguth and Voigt 2003). All the measuring devices used in this study are configured to automatically process the temperature compensation so that all values specified in this text are referring to a temperature of 25 °C.
According to the response times of the sensors the sampling rate is adjusted to 1 metre per

minute. During the first measurement downhole the water column is directly logged in order to reduce the possibility of water disturbances from induced currents by the measuring device. Following a preliminary assessment of the log the levels of depth sampling are determined. Depth samples are collected with a 1.0 L capacity water sampler one day later, allowing time for the borehole chemistry to equilibrate. Directly after sample collection on-the spot parameters such as pH and EC are measured directly with a multi-parameter portable meter (WTW ProfiLine Multi 3320) in the field. All water samples are transferred into containers and, if necessary, treated and condensed for major ion and stable isotope analysis according to DIN 38402-13. Isotope analysis includes measurements of stable isotope ratios of hydrogen, oxygen, dissolved inorganic carbon (DIC) and sulphur.

**Study area**

The Ruhr District, named after the river Ruhr, covers parts of the Federal State of North-Rhine Westphalia (NRW). The Ruhr metropolitan region is the largest urban agglomeration and simultaneously the largest hard coal mining region in Germany. In the beginning of mining activities, the extraction of hard coal was concentrated in the south, where the coal seams crop out directly at the surface (Pfläging 1999). The coal-bearing Carboniferous strata was extensively folded during the Variscan orogeny and reshaped by syn- to post-Variscan break tectonics. North to the river Ruhr, the thickness of the overburden rock increases continuously, and the Carboniferous rocks are unconformably overlain by massive post-Variscan deposits of Late Cretaceous to Quaternary age. According to its extensive distribution, the Upper Cretaceous strata with thicknesses of up to 900 m (Hilden et al. 1995) comprise the most important overburden unit. In the stratigraphical sequence, massive, fissured and local karstified limestones of Cenomanian and Turonian age are overlain by a up to 800 m thick unit called the "Emscher Mergel", Coniacian to lower Santonian clay marlstones (Fig. 1). Beneath the topmost water-impermeable 1 to 2 m, which have been weathered to a clayey silt or silty clay, the clayey marlstone can be fractured and water-bearing to a depth of some 30 to 50 m. Fracturing becomes less common towards the bottom of the zone and finally closes up completely, creating an aquiclude. The Emscher Mergel acts as a major regional seal/aquiclude and separates the deeper groundwater storey of the Cenomanian and Turonian from the upper groundwater storey of the Quaternary and the fractured zone (Melchers et al. 2014).

**Case Study**

Located in the north-western part of the Ruhr District shaft Hermann 1 and shaft Hermann 2 are not influenced by current dewatering measures. They are 1072 m (Hermann 1) and 950 m (Hermann 2) deep, are around 80 m apart and have not been backfilled yet. After evaluation of the available documentation the shafts have already been flooded in 1929. Current water levels are about -230 m NHN[1]. Borehole data reveal total cap rock thicknesses of 800 m. The sequence comprises the Emscher Mergel up to a depth of 600 m followed by Cenomanian and Turonian strata down to a depth of 800 m, which unconformably overlies the bedrock of coal seam-bearing Upper Carboniferous strata. Cenomanian and Turonian beds mainly con-

1 NHN: "Normalhöhennull" ("standard elevation zero") is a standard reference level, the equivalent of sea level, used in Germany to measure height.

sist of fractured limestone and are commonly known as a regional aquifer. Two horizontal working levels for coal mining were built in 850 m and 950 m depth respectively.

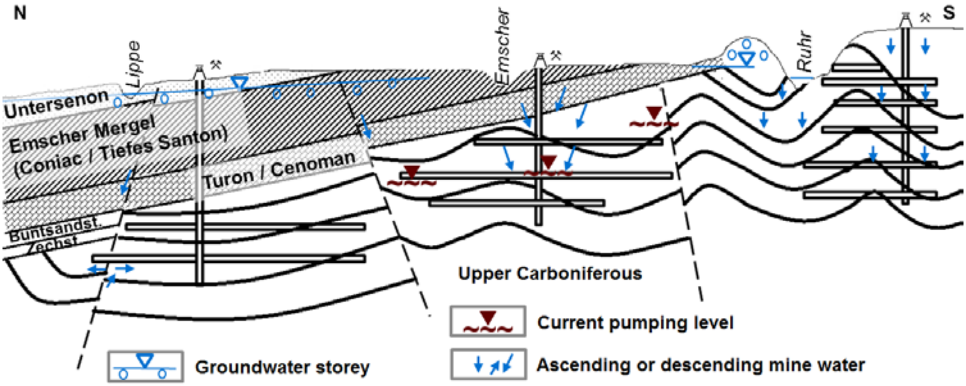


***Figure 1**: Schematic section through the Ruhr coalfield (greatly exaggerated) after Hahne and Schmidt (1982)*

## Results

Figure 2 shows the trend of temperature and EC in the investigated water columns in shaft Hermann 1 and shaft Hermann 2. The dashed line specifies the calculated geothermal gradient of 3.7 °C/100 m after Leonhardt (1983). Additionally, the hydrochemical data indicating the mol% of major ions is presented to the right of the graph in pie charts respectively for the depth from which the samples were collected. Here, all ions which exceed 1 mol% of the total solution content are listed. Up to a depth of 850 m EC and temperature indicate constant values averaging around 9,000 µS/cm and 30 °C. Below 850 m a 1.3 m thick boundary layer follows in which the values increase sharply to an average of 146,000 µS/cm and 41 °C respectively. A brief look at the log provides clear evidence that the temperature distribution within the entire water body does not correlate with the geothermal gradient. Hydrochemically all samples are Na-Cl type fluids with $Na^+$concentration being directly proportional to that of $Cl^-$. All samples of the upper layer still contain traceable concentrations of bicarbonate ($HCO_3^-$) and sulphate ($SO_4^{2-}$) ions. First investigations of stable sulphur isotope data within both shafts reflect the stratification pattern displayed in the geophysical log. The determined $\delta^{34}S$ value for the deeper water body in shaft Hermann 1 is 10.0 ‰ lower compared to the upper water body. All water samples taken from the upper water body show similar values accounting for the homogeneity of the water body between the water surface and 850 m. No stable sulphur isotope value for the dissolved sulphate could be determined for the deeper water body of shaft Hermann 1 due to the low sulphate concentration.

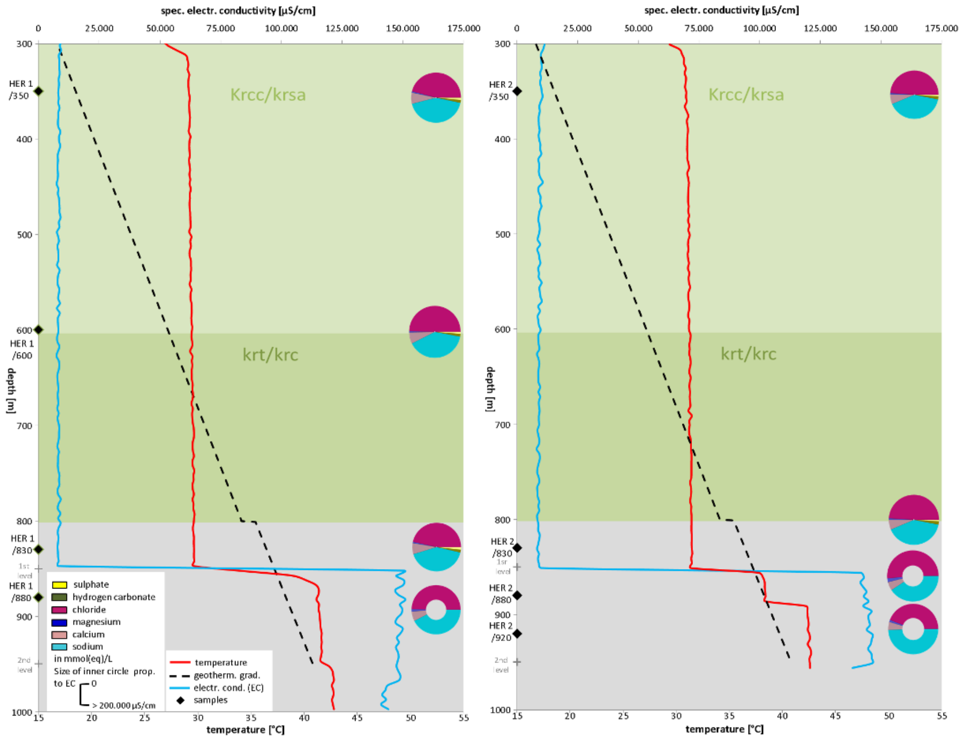


***Figure 2*** *Water quality trend of shaft Hermann 1 (left) and shaft Hermann 2 (right). Depth is indicated in metres below ground surface. Colours indicate lithology (light green: Emscher Mergel, dark green: Cenomanian/Turonian, grey: Carboniferous.*

## Discussion

The formation of density stratification has been identified both in shafts that have already been flooded as well as in shafts that are still undergoing this process. It is obviously not related to the chemical composition of the different fluids, as stratifications are acquired between different water types, such as Na-HCO3- and Na-Cl type fluids, and also between individual Na-Cl type water bodies of different TDS (as it is the case in shaft Hermann 1 and 2). The thickness of homogeneous water bodies can vary from just a few metres to as much as several hundred metres. However, the boundary layer is very distinctive with usually no more than a few decimetres in depth. According to present knowledge the formation of boundary layers is largely based on water inflow from the surrounding rock and on rock-specific properties such as thermal conductivity and fracturing. However, the shaft lining can also play a role here, as this provides the route for water inflow at the individual horizon levels.

Repeated geophysical measurements in shaft Hermann 1 and 2 reveal the formation of stable density stratification. In the water columns of both shafts a sharp boundary layer is located at a depth of 850 m. It is apparent from the documents that the two shafts are connected via the 1st level (850 m-level) in approximately this depth. All hydrochemical and stable isotope data which have been evaluated so far point to an active hydraulic communication over the mine workings and possibly the surrounding rock. Previous studies dealing with this subject considered a temperature-dependent density-driven flow as a reason for this phenomenon (e.g. Gebhart et al. 1988, Melchers 2015, Wolkersdorfer 1996).

The triggering force for this movement is seen in the geothermal gradient. Theoretically, in an underground water column this gradient warms up the deeper-lying mine water and induces convective transport related current phenomena (Berthold 2009). These prevent the mixing of inflows of a different solute composition, which leads to the formation of a further convection cell. Flow velocity measurements in combination with numerical simulations conducted by Kories et al. (2004) revealed numerous circular currents being responsible for the homogeneous conditions within the water body of shaft Hermann 1. In their model current velocities appear to be high in regions of homogeneity and low near the boundary layer. The authors further demonstrated that a continuous fresh water recharge is crucial for a stable stratification. In available records dealing with the Hermann coal mine relatively high quantities of water flowing in from the side-walls during the active production phase are documented. In combination with high underground temperatures and sales problems at the coal market the costs for the drainage forced the early closure of the mine. Latest camera inspections of the upper shaft lining above the water surface in course of on-going monitoring measures point to steady inflow of near-surface water through the brick walls. As a result, the observed conditions plead for a continuous water recharge.

In geochemical terms, the mine water generally equates to a mixture of ground water and soil leachate that has been geochemically altered by the various processes taking place in and around the mine workings. As a result, processes such as gas dissolution and release, evaporation and condensation can alter the solute concentrations within the water column. According to the results of the hydrochemical analysis combined with the regional hydrogeology, the upper water body is subject to exchange reactions with water from the upper as well as with water from the lower groundwater aquifer. Pursuant to the assumption that water exchange between the two water bodies is minimal across the boundary layer, flow of the brine type lower water body in both shafts points to an interaction with the deep formation water of the Carboniferous strata. In order to specify origin and flow path of the water and to assess the associated physicochemical processes affecting the water bodies such as water-rock-interactions, stable isotope geochemical investigations have been performed on all collected samples. The significant difference of 10 ‰ in the stable sulphur isotope data of shaft Hermann 2 indicates an additional sulphur source mixed with the sulphate inventory of meteoric water in the lower water body. We assume that this secondary source with a depleted 34S value stems most likely from organic sulphur in the hard coal. Alternatively, alteration by sulphate reducing bacteria cannot be ruled out. In the future the data has to be interpreted in terms of stable isotope distribution patterns under consideration of calculations concerning the mass balance and equilibrium or kinetic isotope effects. The density differences along with distinct stable sulphur and oxygen isotope signatures of the dissolved sulphate as well as stable carbon isotopes of the DIC help to understand mass flow across the stratification boundary and addresses microbial processes in a first attempt. Stratification patterns in old mine workings play a crucial role in post-mining management regarding disposal and treatment of contaminated waters and need to be monitored. Hence, it can act as a barrier for contaminated mine waters and lower the potential risk of mine water mixing with groundwater reservoirs.

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