

Natural Tracers for Mine Water Fingerprinting – A First Step to a Hydrogeochemical Monitoring Plan for Risk Assessment During Mine Water Rebound in the Ruhr District Area, Germany

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Abstract

Bromide as natural tracer in combination with hydrochemistry and isotope geochemistry has been applied to distinguish regional aquifers from mine water derived from Upper Carboniferous hosted former hard coal mining area in the Ruhr District, Germany. The hydrogeochemical dataset successfully identified different origins of salinity, i.e. halite dissolution vs. seawater evaporation. Cl/Br ratios and molar Na/Cl ratios of mine water differ significantly compared to groundwater in Upper Cretaceous host rocks consisting of Coniacian-Santonian and Cenomanian-Turonian fractured aquifers. The bromide tracer has the potential to be used for risk management purposes during mine water rebound in order to verify containment.

Keywords: Tracers, Hydrochemistry, Mine Water Rebound, Monitoring, Hard Coal

Introduction

Mine water rebound in the former Upper Carboniferous hard coal mining region of the Ruhr Valley is a long-term billion Euro project operated by the former coal mining company Ruhrkohle AG. Since hard coal mining ceased at the end of 2018, the region is on transition to the post mining stage (Melchers *et al.* 2020). In order to manage risk of contamination and accurately forecast mine water rebound water levels, conformance and containment of mine water needs to be frequently monitored. This study aims to provide and develop a hydrogeochemical monitoring toolset using preferentially natural tracers to mitigate any unwanted loss of containment, besides being an ecological feasible and cost effective solution. Upper Carboniferous hosted mine waters, hence, groundwater which came into contact with underground mine workings, are characterized by high salinity and high levels of sulfate and iron species resulting from (di)sulfide oxidation processes within the mine. One of the major tasks in characterizing deep, saline fluid inventories is to identify the origin of salinity. Brine-type, Na-Cl dominated basinal waters can have different origins (Hanor 1994; Kharaka and Hanor 2014). Two major processes are (a)

evaporative pathways of formerly trapped or infiltrated seawater and (b) subsurface dissolution of salt minerals, preferentially halite. Initial seawater composition, i.e., *sensu strictu* connate waters, can be subsequently modified after entrapment by diagenesis, water-rock interaction, microbial interactions and mixing with groundwater in the subsurface.

Geology & Hydrogeological framework

The former coalfield of the Ruhr Valley is situated in folded and weakly metamorphosed Paleozoic basement rock of Upper Carboniferous age referred to as the Rhenish Massif (Kukuk 1938). Upper Carboniferous siliciclastics intercalated with coal measures (Namurian to Westphalian A-C) forms the host rock of the former mining area. The folded Upper Carboniferous strata is gently dipping towards the North. It is unconformably overlain by Mesozoic sediments of the Muensterland Basin, which are dominated by Upper Cretaceous marls and carbonates (Hiss and Mutterlose 2010). These two geological provinces contain both Na-Cl type basinal groundwaters with electric conductivities exceeding 200.000 $\mu\text{S}/\text{cm}$. In the Muensterland Basin, the brine infiltrates

Cenomanian-Turonian strata and builds a regional aquifer extending from the northern edge of the basin, towards the southern border to the Paleozoic basement known as the Haarstrang ridge (Struckmeier 1990). Numerous spas and former saltworks are located in the region and making use of this saline aquifer since mediaeval times. Up to 1500 meters thick, marly sediments of the Emscher Formation, Middle Coniacian to Upper Santonian, were deposited on top of the Cenomanian-Turonian carbonate sequence. The Emscher Formation consists of homogeneous grey to dark grey coloured sediments of finely laminated to thick layered and in parts organic rich (Type II) marls. Hydrogeologically, the Emscher Formation is a thick aquitard whereas its uppermost part includes a local fractured aquifer in the Ruhr District. Enclosed by aquitards, the Cenomanian-Turonian aquifer is confined. Evaporite deposits in the area are represented by Permian (Zechstein) and Triassic (Upper Bunter, Roet Fm.) salt sequences. They were deposited on the northern rim of the Muensterland Basin and along the western margin down to the Lower Rhine region. The Upper Santonian Haltern Formation incl. Recklinghausen Formation overlying the Emscher Formation represents an important drinking water reservoir for the region. Currently, it is necessary for baseline requirements to identify certain waterbodies exhibiting hydrogeochemical fingerprints inherited from different host rocks, i.e. Upper Carboniferous basement, Cenomanian-Turonian or Coniacian-Santonian signatures. It is anticipated that during the main rebound phase mine water will infiltrate the overburden and potentially mix with Cenomanian-Turonian saline aquifer, and subsequently, will rise within the pore network and fault pathways of the Emscher Formation. As prerequisite, Haltern Formation strata as drinking water reservoir must be kept free from mine waters.

Halogen Geochemistry

Halogens, especially bromide (Br⁻), have been used frequently to decipher the origin of brines, but also to distinguish organic matter types with organobromide content

(ten Haven *et al.* 1988). Especially Type II marine organic matter is prone to contain up to 1000 mg/L bromine (Vassilev 2000). Chloride vs. sodium species have been evaluated to further distinguish halite dissolution vs. a general seawater evaporation trend (Kharaka and Hanor 2014). General seawater contains 65 to 67 mg/L bromide, which increases subsequently in the solution during evaporation up to a value of 6000 mg/L (Hanor 1994). During crystallization of halite, bromide is preferentially retained in solution (Braitsch and Herrmann 1963). This fact enables the linkage between bromide concentration to track halite dissolution and evaporation paths of saline fluids.

Methods

Over 200 samples have been collected for hydrogeochemical analyses from 2017 to 2020. Available literature data was reviewed, and quality controlled using general ion balance assessment. Hydrogeochemical analyses of major cations and anions were conducted by certified lab analyses according to DIN ISO 11885 and DIN 10304-1 protocols. As trace elements strontium, barium, boron and bromide species were analysed. Monitored on-site parameters are electric conductivity, pH, ORP, temperature and oxygen content of the water using WTW Multi 3320. Oxygen and hydrogen stable isotope measurements were obtained with an optical analyser (Picarro 2130i, Picarro, Inc., Santa Clara, CA, USA) using the laser-based principle of cavity ringdown spectroscopy. The standard deviation per sample was on average 0.06‰ for $\delta^{18}\text{O}$ and 0.48‰ for $\delta^2\text{H}$.

Results and Discussion

Upper Carboniferous host rock, Upper Cretaceous Cenomanian-Turonian aquifer and Upper Cretaceous overburden section containing mainly Coniacian-Santonian Emscher Formation groundwater have been defined as potential hydrochemical end members. For risk assessment purposes, these three groups need to be characterized using baseline thresholds. In the Piper plot (Fig. 1), most of the analysed samples of Upper Carboniferous mine waters and Cretaceous Cenomanian-Turonian aquifer samples plot

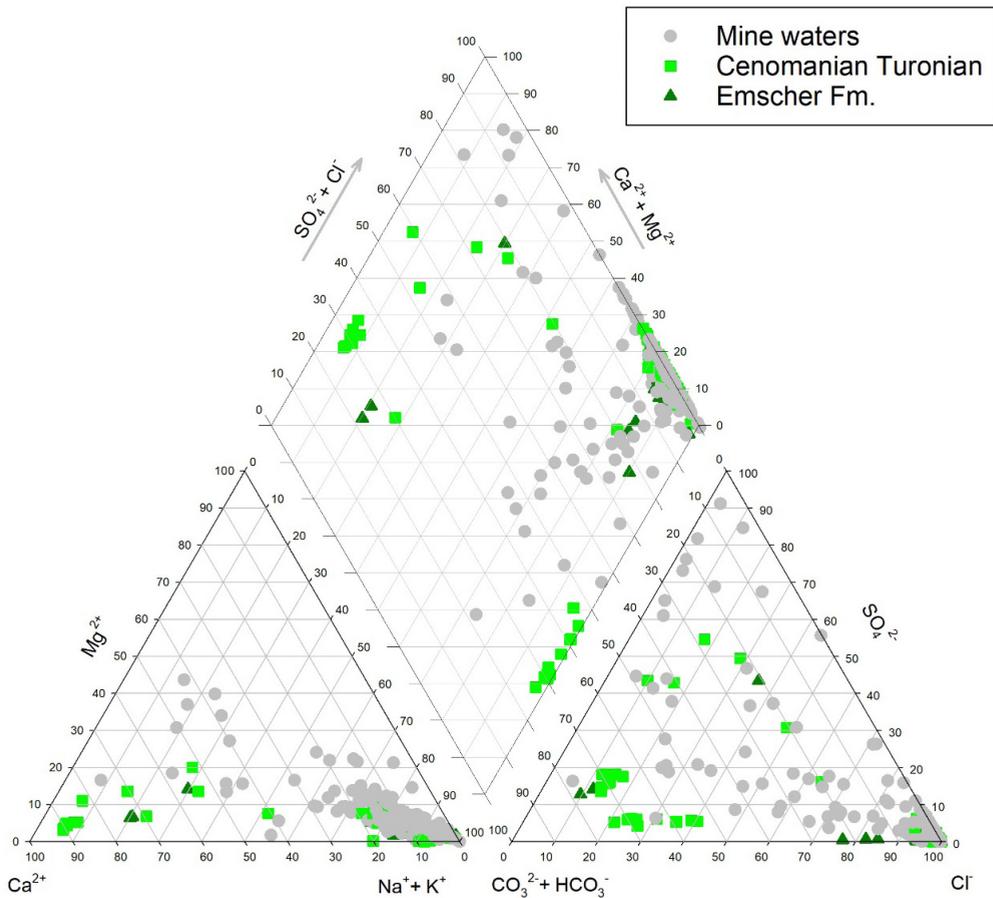


Figure 1 Piper Plot: hydrochemical facies of mine water samples vs. Upper Cretaceous groundwater.

within the diamond plot in the right quadrant being identified as Na-Cl dominant waters. Using major cations and anions distributions of the data yield no clear distinction between the saline aquifers of Upper Cretaceous and Upper Carboniferous hosted mine waters.

Hydrogen and oxygen stable isotopes

The compilation of oxygen and hydrogen isotopes helps to decipher the salinity of groundwater and its origin, because of isotope fractionation processes during evaporation or mixing of various isotope reservoirs (Fig. 2). For comparison, a global (GWML) and local meteoric waterline (LWML) representation (IAEA- GNIP data from the city of Bad Salzflun, Germany) as well as the reference standard V-SMOW and the local Ruhr District meteoric water

signature are included. Grobe & Machel (2002) concluded a mixing trend of present day meteoric water and seawater (SMOW) at that time. However, having compiled $n=213$ samples revealed a trend which levelled off at $\delta^2\text{H} = -20\text{‰}$ towards more positive $\delta^{18}\text{O}$ -values ranging in between $\delta^{18}\text{O} = -4$ to -1‰ for most of the deeper mine waters in the Upper Carboniferous host rocks. Such trend is in agreement with either oxygen exchange reactions or evaporation-recharge. Oxygen exchange reactions result in more positive oxygen isotope uptake, common at elevated temperatures, and respectively for a constant shift towards more positive $\delta^{18}\text{O}$ -values. A freshwater evaporation prior to recharge trend is indicative for affecting both, oxygen and hydrogen isotopes to increase. Upper Cretaceous situated samples and data from

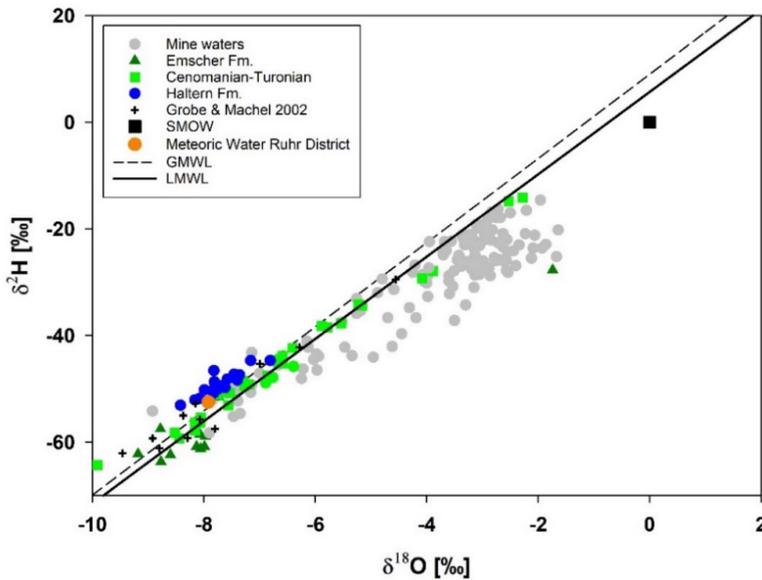


Figure 2 Oxygen and hydrogen stable isotope analysis of mine water samples vs. Upper Cretaceous groundwater; LMWL=Local meteoric water line; GMWL= Global meteoric water line; SMOW=Standard Mean Ocean Water.

spas and springs of the Muensterland Basin plot along the predefined slopes of GWML and LMWL. This data is consistent with data points from Grobe & Machel (2002) and is recognised as modified meteoric waters infiltrating from the North. Lowest values of $\delta^2\text{H} = -58$ to -65‰ and $\delta^{18}\text{O} = -9.9$ to -8‰ are reported preferentially from formation waters of the Emscher Formation.

For comparison, data from the Haltern Formation as major drinking water reservoir exhibit excess deuterium and plots left of the GWML. Excess deuterium values and more negative $\delta^{18}\text{O}$ values compared to the GWML are characteristic for low temperature water-rock interaction and microbial processes. All samples plot significantly below the SMOW reference value and hence are not associated with an evaporative seawater path.

Halogen geochemistry

In Figure 3 molar concentrations of sodium vs. chloride ions are plotted. The data trend indicates either halite dissolution having a linear correlation with an ideal slope of $\text{mNa}/\text{mCl} = 1$ compared to a linear trend of seawater evaporation which corresponds to a slope value of $\text{mNa}/\text{mCl} = 0.86$.

As already suggested by Wedewardt (1995) and Grobe & Machel (2002), saline groundwater from Cenomanian Turonian aquifer system plot on the Na/Cl slope = 1 line as well as samples from the western part of the Ruhr District. Upper Carboniferous mine waters as well as formation waters from the Emscher Formation instead plot on the classical seawater evaporation trajectory (SET). Their formation waters are related to ancient evaporated and modified seawater trapped as porewater. Halite dissolution initiated by meteoric water infiltration is the obvious scenario for the saline waters of the Cenomanian-Turonian aquifer system and has been confirmed with the larger data trend.

Figure 4 illustrates a log-log cross plot of bromide vs. chloride mass concentration ratios. Modern seawater ratio which exhibits a value of $\text{Cl}/\text{Br}=288$ has been implemented as reference and starting point of SET. Wedewardt (1995)'s subset of mine waters range from $\text{Cl}/\text{Br}=350$ to $\text{Cl}/\text{Br}=1450$ values with a mean of $\text{Cl}/\text{Br}=789$. Cl/Br values >1500 were sampled within the mine workings by the authors but are often associated with Upper Cretaceous sourced groundwater. Especially samples from easternmost collie-

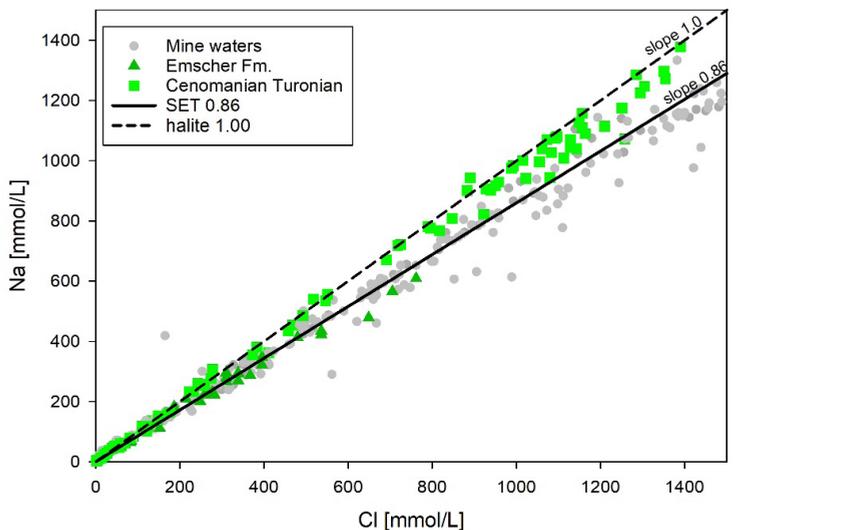


Figure 3 Molar concentrations of chloride and sodium of mine water samples vs. Upper Cretaceous groundwater; SET 0.86=seawater evaporation trajectory; halite 1.00= halite dissolution line.

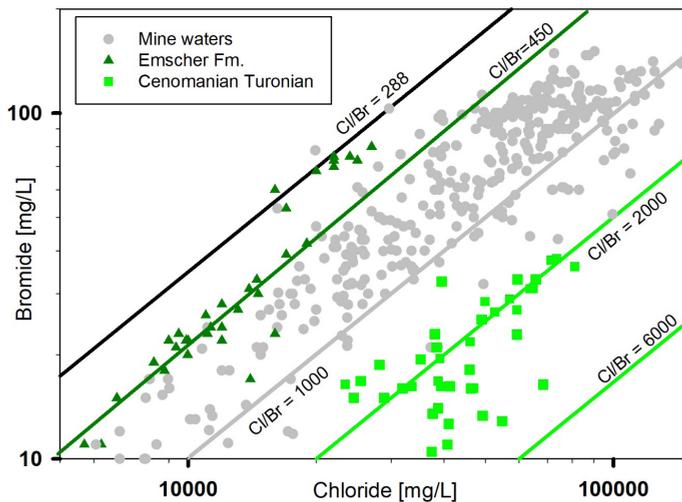


Figure 4 Log-Log-plot of bromide vs. chloride mass concentrations of mine water vs. Upper Cretaceous groundwater.

ries exhibit such high Cl/Br data within the mine. On the other hand, mine water in collieries from the western border of the Ruhr District show anomalously high Cl/Br values, which correspond to halite dissolution from Zechstein formations in the vicinity. Emscher Formation strata hosted groundwater generally has Cl/Br <450 values. Two samples report even higher Cl/Br ratios

than seawater. The Cenomanian-Turonian aquifer system including various samples from spas and springs in the Muensterland Basin which were preferentially sourced by this water consistently corresponds to Br/Cl ratios >2000. Br/Cl ratios with values in between 1500 to 2000 are closely associated with mines and indicate mixing of the two prominent saline aquifers.

Conclusions

The dataset reveals that the hydrochemistry of the Cenomanian-Turonian regional aquifer in the Muensterland Basin stems from modified meteoric water due to halite dissolution – as has been suggested by former researchers (Grobe and Machel 2002; Wedewardt 1995). Mine waters have their own distinctive Cl/Br pattern derived from Upper Carboniferous formation water modified due to water rock interaction and coal maturation. Emscher Formation hosted groundwater exhibit anomalous high bromide concentrations most likely due to organobromide contribution from organic matter type II. The dataset identifies water bodies modified by halite dissolution from Zechstein in the western part and is able to differentiate groundwater from Emscher Formation, Cenomanian-Turonian aquifer and mine water in the eastern part of the Ruhr District. As follow-up project, we will compare the hydrochemical data with additional trace element data including lithium and strontium.

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