Natural Tracers For Mine Water Fingerprinting III – an Approach to Identify Mine Waters from Distinct Mine Water Provinces during Mine Water Rebound in the Ruhr District Area

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Abstract

This long-term hydrogeochemical research initiative associated with the mine water rebound in the former hard coal mining area of the Ruhr District, Germany, aims to characterize specific water bodies in the mine water provinces as a major prerequisite for a sustainable and controlled rebound process. A combined natural tracer approach has been applied and comprises classical major cation/anion species analyses, inorganic tracer compounds (Cl^-/Br^-, Li^+,) as well as stable and radiogenic isotope geochemistry measurements (δD, $\delta^{18}O$, $^{87}Sr/^{86}Sr$). Here, we focus on detailed test cases for the bromide tracer. In order to assess the bromide (Cl^-/Br^-) tracer's precision and limitations as the most prolific and ubiquitous tracer in this multi-tracer approach, it has been evaluated for single colliery mine workings and adjacent mine water compartments to identify separate mine water bodies. Examples comprise the mine workings of the colliery Prosper Haniel and adjacent mine workings in the northern part and a dataset in the eastern part of the former mining area. The latter has been partly infiltrated by aquifers and formation waters of the Upper Cretaceous overburden section. Shaft profiles with a multi-parameter probe were able to identify separate water bodies at depth in the eastern province. The bromide tracer exhibits very narrow ranges within the water provinces in the Ruhr District mining area and hence, was able to identify water bodies from distinct mine workings and water provinces. In the eastern part, where in isolated water provinces the mine water rebound is very mature, an already infiltrated mixture of mine water with the overburden formation waters was identified. This data based on "geochemical-independent" natural tracers aims to build a foundation for a robust integrated risk management approach accompanying the rebound process in the Ruhr District.

Keywords: Mine water, hard coal, Ruhr district, tracer, risk management

Introduction

After mine closure, mine water management associated with mine water rebound becomes increasingly difficult due to limited access to the underground mine workings. Apart from major dewatering stations and backup stations as well as a vertical pipe network acting as piezometers and methane degassing facilities implemented into shafts, there remains no direct accessibility to the underground mine workings anymore. This limited access is a major issue to study mine water hydrogeochemistry and hydrodynamics. For risk management purposes and hence, to ensure a sustainable and controlled mine water rebound process, a profound monitoring system including a detailed hydrochemical assessment of mine waters and surrounding aquifers is therefore essential. It leads to thorough understanding of the mine water and regional hydrology and builds a foundation for benchmarking and modelling. Therefore, it helps to mitigate or even overcome this accessibility obstacle during the rebound process.

This research is a continuation of a first and second assessment on mine water hydrogeochemistry and regional hydrogeology (Jasnowski-Peters & Melchers 2021 & 2022) as well as former shaft depth

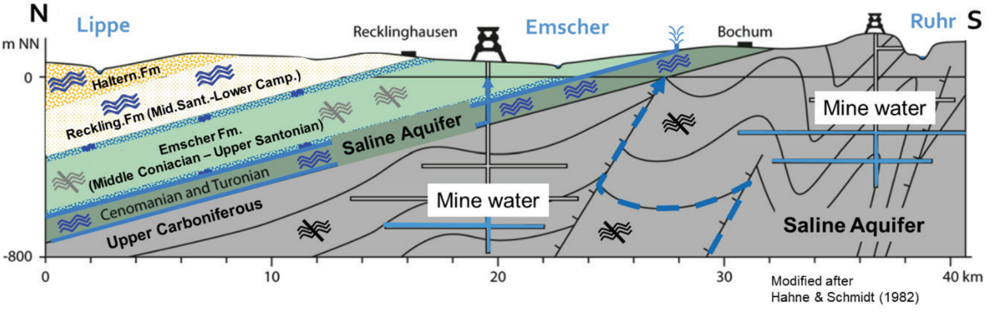

Figure 1 Generalized cross section of Rhenish Massif to south western Muensterland Basin; Upper Carboniferous strata with coal measures gently dipping towards the North, unconformably overlain by Upper Cretaceous marls and carbonates; the regional saline aquifer is situated within Cenomanian to Turonian fractured carbonates which is overlain by marly to clayish strata of up to 1500m called Emscher Formation. Drinking water reservoirs consists of fine calcareous sandstones of Haltern Fm. pinching out close to the river Lippe (modified after Hahne & Schmidt 1982)

profiling using a multi probe setup (Henkel & Melchers 2017). Major aim was to identify useful natural tracers within the mine water hydrochemistry, which identifies mine waters and its mixtures from adjacent aquifers in the overburden section during rebound. Bromide (Br^-) has been found so far to be able to act as a profound tracer as it is ubiquitous present in measurable amounts and is very conservative in its geochemical behaviour. Mixtures of mine water with regional aquifers cannot be excluded when mine water level rises up reaching the overburden rocks, which consists of Upper Cretaceous marls and carbonates (Fig.1). Here, we closely evaluated the bromide tracer normalized to chloride concentrations (Cl^-/Br^-) within mine waters and adjacent aquifers to test its suitability for identifying single distinct water bodies within the extensive mine workings network in order to track them during rebound.

Is there a geochemical fingerprint based on the chloride to bromide tracer, which is related to a gradient within the host formation of Upper Carboniferous strata or a regional hydrogeological fingerprint related to overburden thickness and various formation waters and aquifers influencing the Upper Carboniferous mine waters in the past?

The dimensions of the entire mine workings network in the Ruhr district is about 5000 km2. In the past, Permian (Zechstein) sourced waters and Upper Cretaceous saline waters from the regional Cenomanian-Turonian aquifer situated near the base of the overburden rocks already infiltrated Upper Carboniferous strata and mixed with hosted mine waters. In the eastern part, an influence of formation waters of the Emscher Formation, which can mimic mine waters as it hosts a lot of framboidal pyrite, is apparent. Such candidates of already mixed waters with fingerprints of the various water bodies in the overburden section need to be identified. In the eastern part of the Ruhr District tectonically isolated mine water provinces exists adjacent to central ones taking part of the rebound. In the isolated mine water provinces, mine water rebound has already been accomplished with mine waters rising close to the surface. Such showcases might act as a natural laboratory for the future major rebound.

A case study of water samples from shafts and surrounding mine workings of adjacent collieries will be presented here in order to have a closer look, if the bromide (Br^-) tracer is still valuable for identifying such mixing with different formation waters of the overburden (Fig.2).

Methods

Hydrogeochemical analyses of major cations and anions were conducted by certified lab analyses according to DIN ISO 11885 and DIN 10304- 1 protocols. Trace elements included barium, boron, bromide, fluoride, lithium, strontium and various transition metals. Bromide concentrations were measured using ion chromatography combined with UV

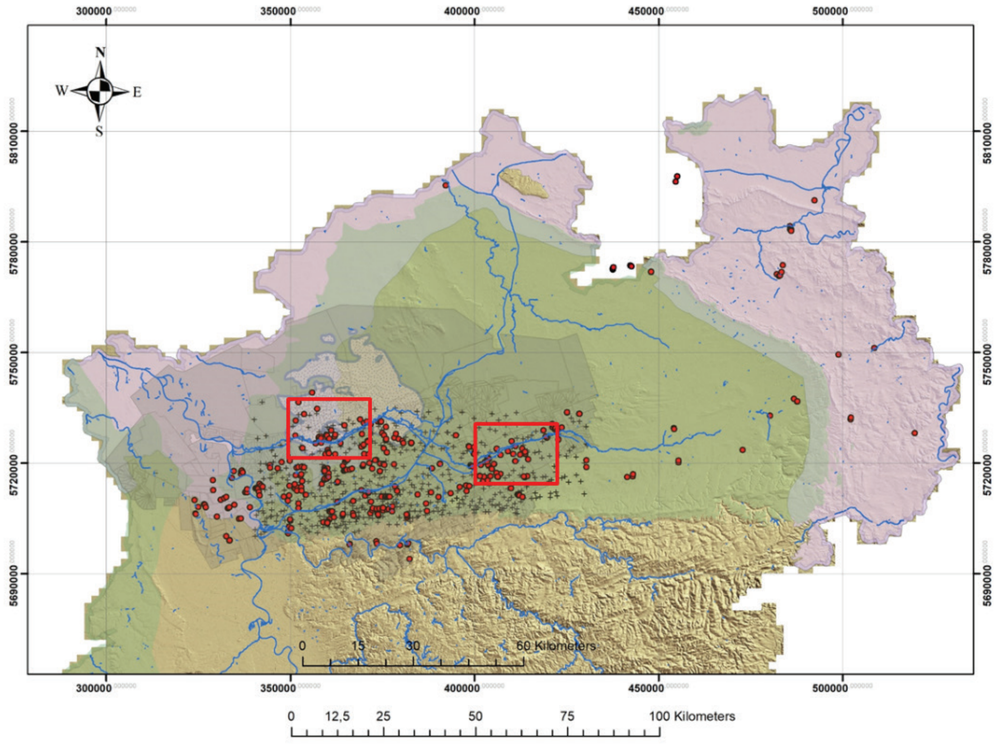

***Figure 2** Overview of mine area concessions (shaded bright green) of the Ruhr District on a bedrock geological map; the extent of Upper Cretaceous sediments (green) and of saline formations (magenta), i.e. Permian Zechstein and Upper Bunter Roet Fm. Are highlighted; red dots are mine water sample locations; crosshairs mark shaft locations; red rectangles mark the two areas of case studies in the northern and eastern part of the Ruhr District hard coal mining area*

detection in order to be not influenced by high chloride concentrations.

Results

A more accurate test for chloride to bromide ratio as tracer has been conducted using water samples taken during depth profiling of flooded vertical shafts in isolated mine water compartments of the eastern part of the mine area together with historical water samples from adjacent collieries. Former degassing and monitoring (plumbing) pipes in direct exchange with shaft related mine waters have been used for discrete depth water sampling. The shaft profiles have been formerly investigated using a multi-diver-probe setup measuring continuously electrical conductivity, temperature, ORP and pH in order to identify potential density stratifications and convection cells (Henkel & Melchers, 2017). Cl^-/Br^- ratios of discrete depth water samples from shafts with known lithostratigraphic correlation have been plotted together with historical water samples taken during mine operations at adjacent mine workings in a log-log plot based on mass concentrations (Fig.3). In Fig. 3, mine waters hosted in Upper Carboniferous strata vs. Upper Cretaceous formation water samples were subdivided in order to highlight the sharp boundary between the two major water body signatures. Chloride to bromide ratios in the range of 300 to 1000 have been recorded in the data. There is a good spread of data of higher bromide containing and less saline water samples from Upper Cretaceous sources with high saline less bromide-rich mine water samples. Cl^-/Br^- ratios of <600 can be related to formation water signatures of the Emscher Formation which makes up most of the overburden, whereas mine water influenced waters range up to Cl^-/Br^- ratios of 1000. Formerly, the boundary has been set more conservative to be Cl^-/Br ratio <450. The sharp boundary of the two compartments can be related to former density stratifications.

In Fig. 4 a closer look at the dataset from Fig. 3 is presented in adding detailed mine locations of the data points. It is remarkable that single shafts like Waltrop and Koenigsborn (incl. KB LT and KB EG) or single boreholes like Waltrop 2 as well as groundwater monitoring wells like Landwehr/Ost, Stuckenbusch exhibit distinct chloride to bromide ratios. The shaft profile at Koenigsborn sets the boundary for chloride to bromide ratios. It distinguishes between the water bodies more influenced by overburden lithology of the Emscher Formation and the Upper Carboniferous hosted mine waters in the former mine workings (green dots). Potential outliers (blue dots in the lower left corner of the graph) with higher Cl^-/Br^- ratio of >850 might be influenced by the Cenomanian-Turonian saline aquifer contributions leading to much lower bromide concentrations. The dataset from Haus Aden identifies two locations, which have been already infiltrated by waters from the overburden rocks of the Emscher Formation indicated by higher chloride to bromide concentrations due to higher bromide contents affiliated with bromide contributions from organic material.

The second test case focuses on a dataset from the northern part of the Ruhr District in which mine waters exclusively hosted in former mine workings of the colliery Prosper Haniel were assessed. In Fig. 5, mine waters from the colliery Prosper Haniel comprise various mine water samples from the last 30 years including own data acquired in 2019. The data exhibit a very narrow range of chloride to bromide ratios, which level off at very high chloride concentrations. Own acquired data (grey dots) which range from 40.000 to 100.000 mg/L chloride concentrations indicate a similar trend. Explanation for such a trend range from analytical errors using no UV detection for bromide, that bromide reaches a saturation at chloride levels of 100.000 mg/L or more or, if the trend is real, then it can be related to incremental amounts of halite dissolution waters from Zechstein strata mixed with mine waters. Zechstein strata crop out closely to the extent of mine workings from Prosper Haniel and have been clearly identified in relation to large fault lines with offsets of up to 200 meters.

In Fig. 6, the original concentrations of bromide to chloride in the mine water samples are plotted. Two trends can be

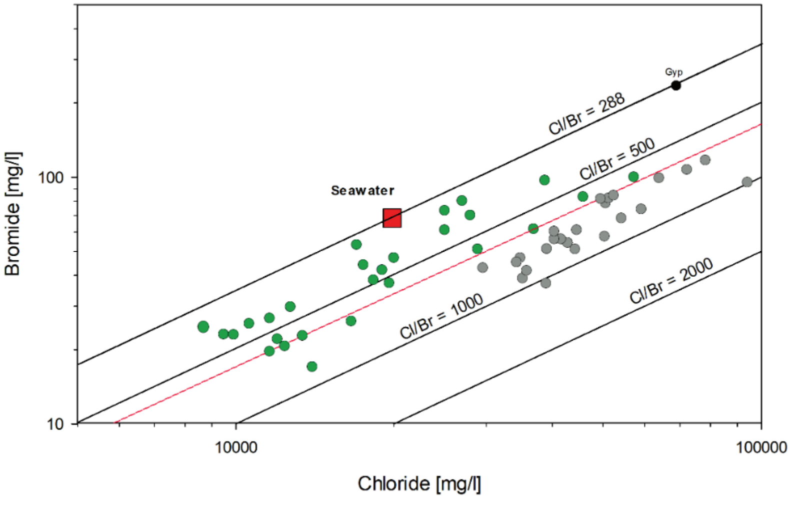

Figure 3 *Chloride to bromide mass concentrations plotted in a log-log plot; water samples from shafts and samples from adjacent collieries are compared with overburden samples. The data consists of Upper Cretaceous lithostratigraphic horizons (green dots) and Upper Carboniferous hosted mine waters (grey dots); red rectangle marks the chloride to bromide content of seawater.*

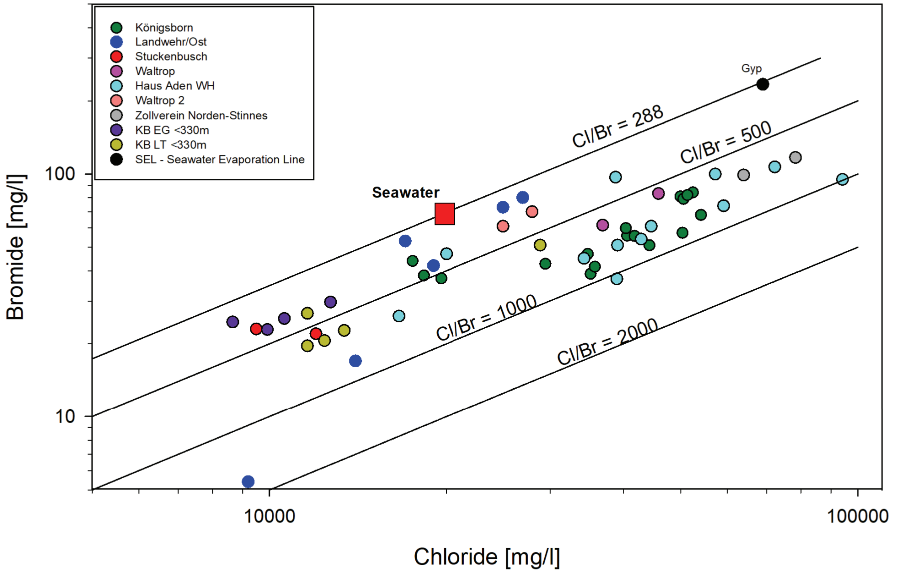

Figure 4 *Detailed origin of water samples including mine and formation waters of Fig. 3.*

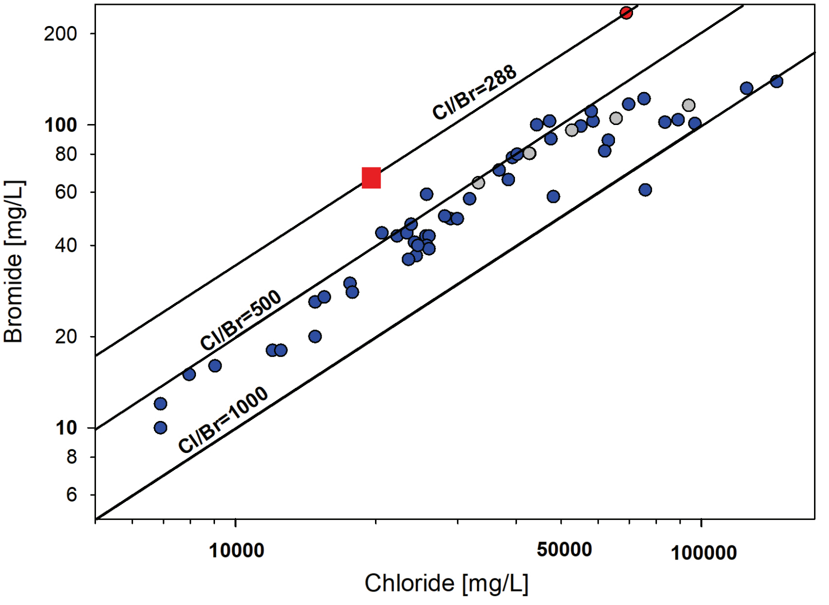

Figure 5 *Mine water samples from the mine workings associated with the colliery Prosper Haniel located in the northern part of the Ruhr District; own data (grey samples) were taken in 2019 at depths from 800 to 1400 meters; historical data (blue dots) were gathered during the last 30 years; red square and red dot marks seawater composition and evaporation path.*

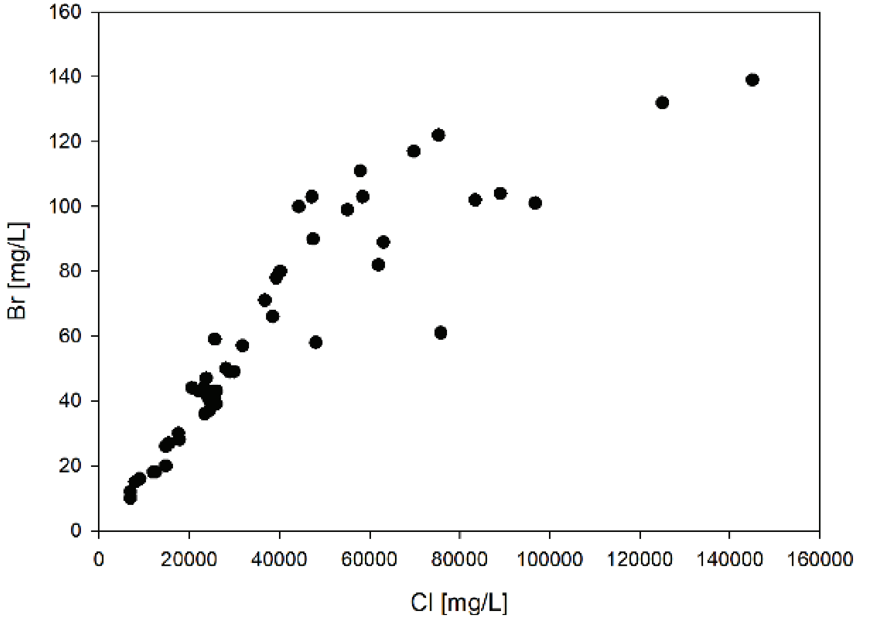

Figure 6 *Original, non-normalized bromide and chloride concentrations in [mg/L] of the mine water samples plotted in Fig. 5.*

identified at chloride concentrations > 60.000 mg/L. A linear trend of Late Carboniferous hosted mine waters and a trend of higher chloride concentration, which add very little bromide concentration and could resemble additions of halite dissolution originated waters like Zechstein waters.

Conclusions

The already tested chloride to bromide ratio as a useful tracer to distinguish mine water brines from saline aquifers has been further evaluated on two distinct water provinces in the Ruhr Valley. The two water provinces are: (1) Prosper Haniel, the last colliery decommissioned at the end of 2018, and (2) the isolated water province of Koenigsborn, for which the mine water rebound has already taken place adjacent to the active one at Haus Aden, which just started its mine water rebound with a mine water level at 1000 meters depth. The ratio that marks the boundary between Upper Cretaceous sourced waters from Emscher Fm. vs. mine waters had a better precision with Cl^-/Br^- ratios of <600 compared to previous data in the subset. The chloride to bromide ratio was successfully tested to distinguish formation waters from the Emscher Formation compared to pristine mine waters and the mixture of both. Similar sulphide oxidation processes for mine waters were recognized in the formation waters of the Emscher Formation due to ubiquitous framboidal pyrite in the strata. This leads to a sulphate rich formation water, which could very much resemble original mine waters of the Upper Carboniferous mine workings and result in false positive alarms associated with the monitoring scheme. Bromide tracer might elucidate such cases and mitigate false positive alarms. For the subset of mine water samples at the colliery Prosper Haniel, the bromide tracer exhibited a narrow range of chloride to bromide concentrations up to very high chloride concentrations. The bromide content indicated a higher spread of values at >80 mg/L bromide content for which the addition of formation waters from Permian Zechstein strata is a plausible scenario. The bromide/chloride tracer is a suitable candidate to be included in risk management and monitoring strategies for the future rebound management of the operator RAG AG and the control measures of the District Council of North Rhine Westphalia. The evaluation will continue to apply sophisticated statistical tools in order to better quantify the various groundwater origins in the future.

Acknowledgements

The authors thank the foundation "Forum Bergbau und Wasser" for financial support. RAG AG is thanked for data access and site support. Laura Cebula is very much thanked for valuable discussions, extensive support during fieldwork and data pre-work of this study.

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