

Natural Tracers for Mine Water Fingerprinting II – a Multi Tracer Approach to Unravel Underground Fluid Movements during Mine Water Rebound in the Ruhr District Area

Henning Jasnowski-Peters, Christian Melchers

Research Center of Post Mining, Technische Hochschule Georg Agricola University, Herner Str. 45, 44787 Bochum, Germany, henning.peters@thga.de

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. For the first time, a combined natural tracer approach comprises classical major cation/anion species analyses, inorganic tracer compounds (Cl⁻/Br⁻, Li⁺), as well as stable and radiogenic isotope geochemistry measurements (δD , $\delta^{18}O$, $^{87}Sr/^{86}Sr$). This data based on “geochemical-independent” natural tracers aims to build a foundation for a robust integrated risk management approach accompanying the rebound process.

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 inevitable. 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 assessment on mine water hydrogeochemistry and regional hydrogeology (Jasnowski-Peters & Melchers 2021) as well as former shaft depth

profiling using a multi probe setup (Henkel & Melchers 2017). The major aim was to identify useful natural tracers within the mine water hydrochemistry, which identification of 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. Mixtures of mine water with regional aquifers can't be excluded when mine water level rises to the overburden rocks which consist of Upper Cretaceous marls and carbonates (Fig.1). Here, we extended the evaluation of dissolved species within mine waters and adjacent aquifers to build a foundation to identify various water bodies within the extensive mine workings network in the future and track them during rebound. The dimensions of the mine workings network 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. Such candidates of already mixed waters need to be identified. In the eastern part of the Ruhr District tectonically isolated mine water provinces exist adjacent

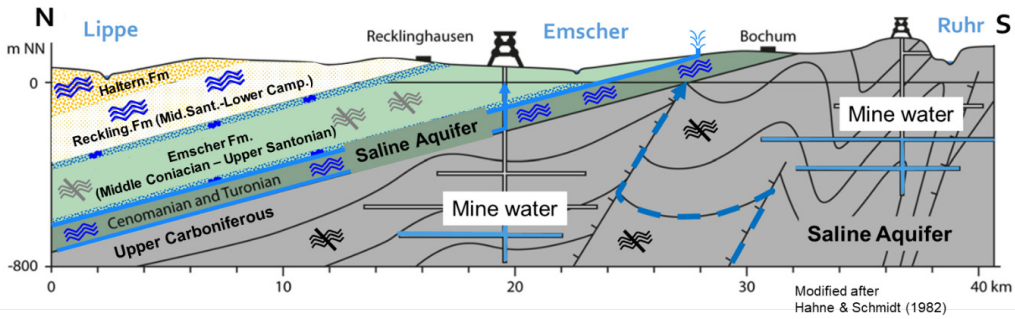


Figure 1 Generalized cross section of Rhenish Massif to south western Muensterland Basin; Upper Carboniferous strata with coal measures gently dipping towards the North, unconformably overlain by Upper Cretaceous marls and carbonates; the regional saline aquifer is situated within Cenomanian to Turonian 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).

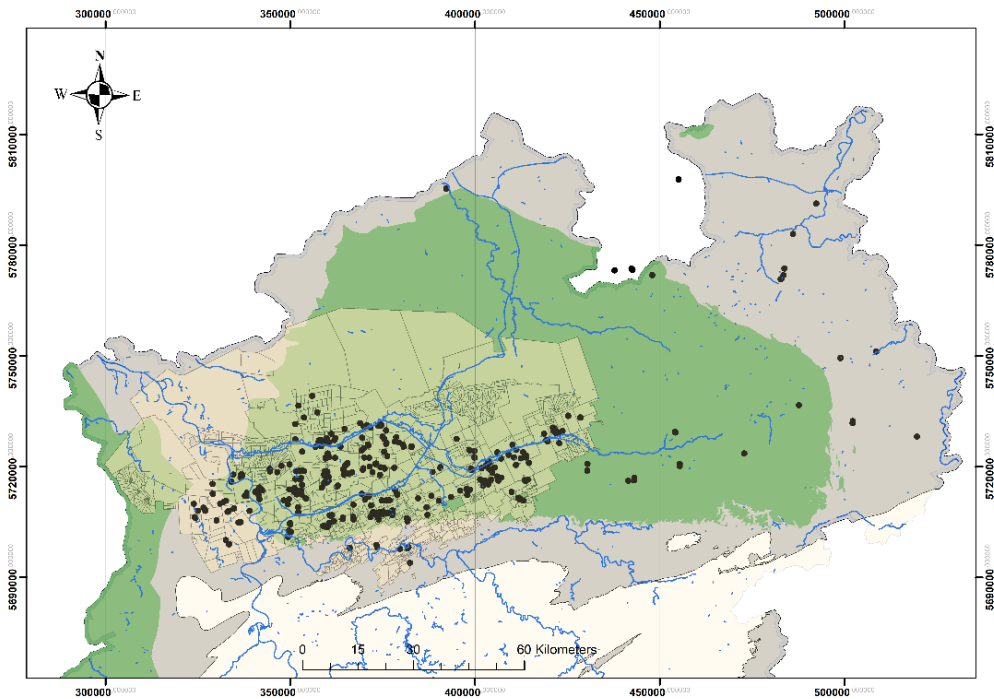


Figure 2 Overview of mine area concessions (shaded bright green) on a bedrock geological maps highlighting the extent of Upper Cretaceous sediments (green); black dots are sampling locations; red rectangle marks area of case study in the eastern part of the Ruhr District hardcoal mining area.

to central ones taking part in 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 is 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). Further assessment of lithium (Li^+) and radiogenic strontium isotopes $^{87}\text{Sr}/^{86}\text{Sr}$ are potential candidates to further distinguish mine waters in the subsurface. These tracers will be evaluated here qualitatively.

Lithium (Li^+) is a lithophilic element with an ionic radius of 0.79 and substitutes scarcely for sodium (Na^+) in crystal lattices, because sodium has a much higher ionic radius of 0.99. Li^+ resembles Br^- in that behaviour. Li^+ does accumulate in residual brines during seawater evaporation and hence can be regarded as a conservative tracer. The concentration range of lithium in formation waters is ranged from 0.04 to 400 mg/L and generally increased with salinity (Dugamin *et al.* 2021). In comparison, river water and seawater exhibit low lithium concentrations of <0.1 mg/L and 0.17-0.19 mg/L respectively. Lithium can be enriched in the formation waters due to water rock interactions. Clays and carbonates play a role in exchanging lithium to the formation water. Subdivided by age, Permian formation waters are indicated by very low lithium concentrations compared to Upper Carboniferous formation waters, which is a good prerequisite to work as a distinguishing tracer (Dugamin *et al.* 2021).

Strontium (Sr) is an alkaline-earth metal and known for its trace element behaviour in most rocks, sediments and waters (Burke *et al.* 1982; Banner 1995). The divalent strontium has a similar ionic radius and charge as calcium and therefore, behaves similarly to calcium and is a common substitute. Strontium concentrations are high in carbonates (on avg. 600 mg/L), evaporites containing gypsum and anhydrite and especially aragonitic carbonates with up to 1 wt. %. Strontium isotopes reported as $^{87}\text{Sr}/^{86}\text{Sr}$ ratio ranges in Phanerozoic seawater from 0.7068 to 0.7092 during the Phanerozoic (McArthur *et al.* 2001). A narrower and very accurate range of Sr isotopes consists for the Late Cretaceous period due to the high density of data. Here, Sr isotopes range from 0.7073 to 0.7076 during Cenomanian to Campanian times and up to 0.708 at the C/T boundary (Jones *et al.* 1994). Hydrothermal waters and deep basinal brines generally exhibit higher strontium isotope concentrations compared to Phanerozoic seawater, because of intense

water-rock interaction, potassium-bearing mineral transformations and, therefore, higher radiogenic ^{87}Sr contributions derived from ^{87}Rb decay.

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.

Lithium has been measured with higher accuracy using an ICP-OES (inductive coupled plasma-optical emission spectroscopy) system in axial geometry in the hydrogeochemical labs of the Geological Survey of North Rhine Westphalia. An already HNO_3 acidified sample was diluted for the appropriate linear concentration range and measured in duplicate. Standards of lithium solution with a known concentration of $\text{Li}^+=1.96$ mg/L and internal water standards as triplets were added after ten sample injections. Accuracy has been determined to be < 5 $\mu\text{g/L}$.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratio was measured with a Thermal Ionisation Mass Spectrometer (TIMS) TI-Box (formerly MAT 262; Spectromat) setup at the Ruhr University of Bochum. PFA columns filled with TRISKEM Sr ion exchange resin (100-150 mesh). Samples were evaporated on a hot plate at 90°C, re-dissolved in 1 ml of H_2O_2 - HNO_3 (1:1;30%:65%) to remove organic remains. Samples were again evaporated on a hotplate and re-dissolved in 0.4 ml of 6M HCl, finally re-dissolved in 1 μl of ionization-enhancing solution and loaded on Re single filaments. Loading, column and reagent blanks as follows: <5 pg, <1 ng, and <0.01 $\mu\text{g/L}$.

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. 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. Cl^-/Br^- ratios of discrete depth water samples with known lithostratigraphic correlation have been plotted in a log-log plot based on mass concentrations (Fig.3). 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 conservatively to be Cl^-/Br^- ratio <450 . The sharp boundary of the two compartments can be related to former density stratifications. A potential outlier with a higher Cl^-/Br^- ratio of >850 might be influenced by the Cenomanian-Turonian saline aquifer contributions leading to much lower bromide concentrations.

Li^+ concentration has been compared to salinity in Fig.4. In the lower range of Li^+ concentration, there is a remarkable fit ($r^2=0,996$) of mine water samples from the major part of the Ruhr District. However, in comparison to basinal samples of a more northern water province within the mine district, Li^+ concentrations differ considerably. The reason is addition of Zechstein based waters in that area which lowers the Li^+ concentration in the samples leading to a much lesser slope in the graph.

Sr isotopes have been measured for various water samples including mine waters, shaft related mine waters, Upper Cretaceous formation waters, regional Cenomanian Turonian aquifer, Muensterland spa and Haltern Fm. drinking water reservoir (Fig.5). Regarding the shaft depth profiles, Sr isotopes reveal a mixing curve of Upper Cretaceous sourced waters and Upper Carboniferous mine waters. Mine waters from the mine water provinces range from $^{87}\text{Sr}/^{86}\text{Sr} = 0.7095$ to 0.7105 and therefore, have values well above the general Phanerozoic seawater distribution. A trend in one of the northern water provinces indicate a mixing curve of Upper Carboniferous hosted mine waters

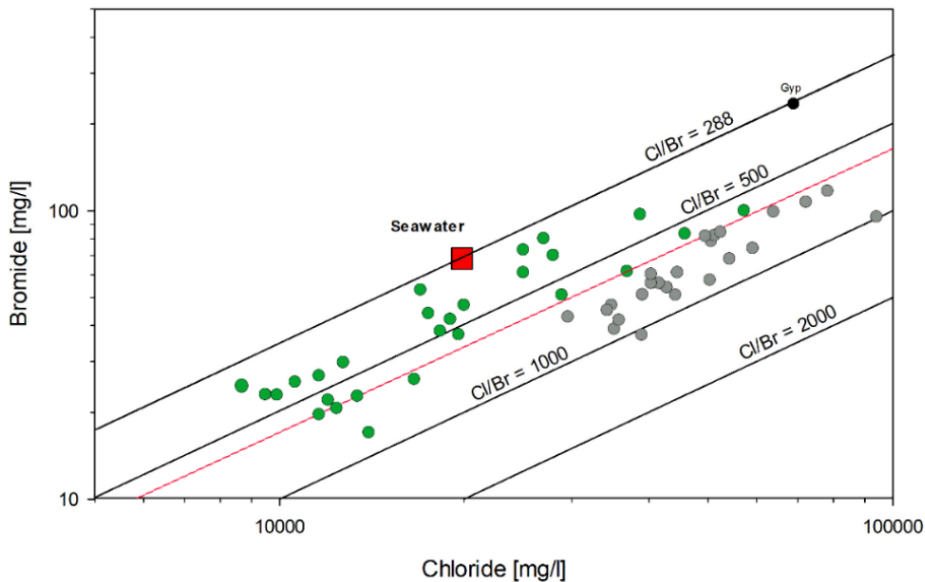


Figure 3 Chloride to bromide mass concentrations plotted in a log-log plot; mine water samples from shafts and samples from adjacent collieries are compared. The data consists of Upper Cretaceous lithostratigraphic horizons (green dots) and Upper Carboniferous hosted mine waters (grey dots).

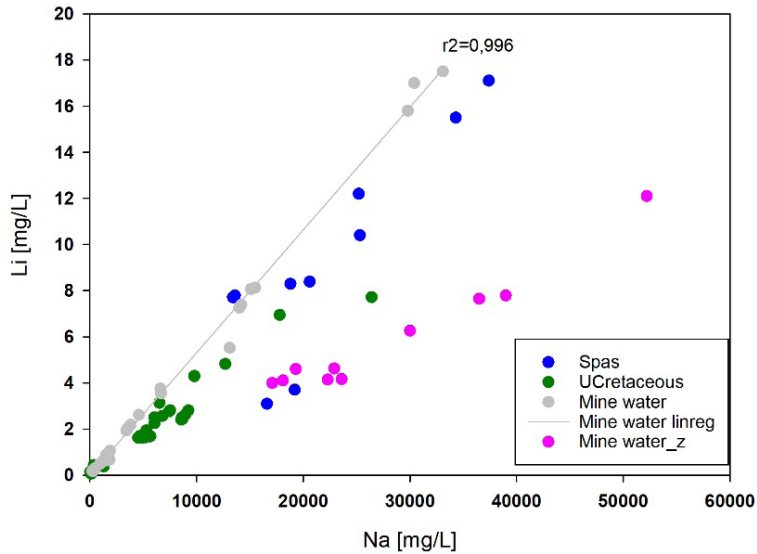


Figure 4 Lithium (Li^+) concentration vs. sodium (Na^+) concentration reported for Upper Cretaceous derived samples (green dots) and mine waters (grey dots); mine waters have been further subdivided to Permian (Zechstein) sourced waters within the data (pink dots); For comparison, deep seated samples from spas in the Muensterland Basin have been added (blue dots).

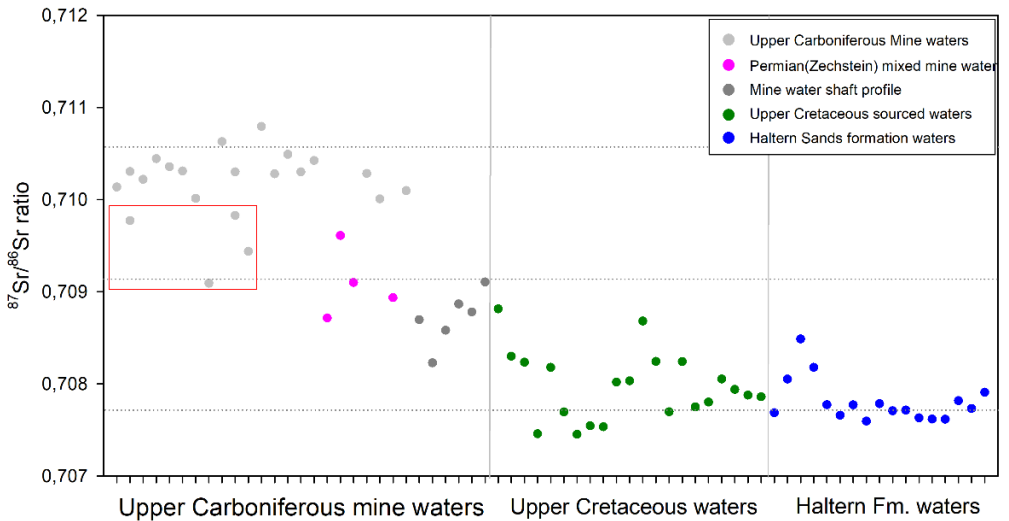


Figure 5 Strontium isotope ($^{87}Sr/^{86}Sr$) plotted vs. various groundwaters; data include Upper Carboniferous mine waters (grey dots) and Permian(Zechstein) mixed mine waters (pink dots), a shaft profile (dark grey dots), Upper Cretaceous sourced waters and Haltern Fm. (“Haltern Sands”) formation waters.

with Permian(Zechstein) contributions. Very low $^{87}Sr/^{86}Sr$ signatures down to 0.707 mark Permian sourced waters. Hence, mixing of Zechstein based waters lead to a lower overall ratio of Sr isotopes indicated by a range of $^{87}Sr/^{86}Sr = 0.7087$ to 0.7103. Similar to the

Li/Cl concentrations, Zechstein based fluid signatures are highlighted in the data.

True mine water samples with no admixtures of different formation waters of the surrounding strata are well defined with Sr isotope signatures of $^{87}Sr/^{86}Sr = 0.710$ -

0.711. Lower Sr isotope values indicate some admixtures of either Upper Cretaceous or Permian (Zechstein) based fluids as indicated in pink and dark grey (Fig.5). The mine shaft profile marked with dark grey dots grade from a continuous record of Upper Cretaceous overburden section to higher contributions of Upper Carboniferous sourced "true" mine waters. Mine waters in the graph indicated within the red rectangle have low electrical conductivities and show minor contributions from overburden sourced waters.

Conclusions

A useful addition of lithium concentrations and strontium isotopes as natural tracers to build up a tracer inventory for hydrogeochemical monitoring has been evaluated. The already tested chloride to bromide ratio as a useful tracer to distinguish mine water brines from saline aquifers has been further evaluated on shaft depth profiles, where mine water rebound has already taken place. 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. The chloride to bromide ratio was successfully tested to distinguish formation waters from the Emscher Formation compared to mine waters due to a sharp boundary. Similar sulphide oxidation processes for mine waters were recognized in the Emscher formation. This might lead to a sulfate rich formation water which could result in false positive alarms associated with the monitoring scheme. Bromide tracer might elucidate such cases and mitigate false positive alarms. Lithium as a cation behaves similarly to bromide and can be used from very dilute samples up to brine type waters to type mine waters. In the case of mine waters, lithium has a remarkable linear correlation coefficient comparing it to sodium cations, i.e. salinity. Strontium isotopes as a well known tracer for numerous hydrological studies have proven a valuable addition to the tracer mix. For the Upper Cretaceous, the existing record on strontium isotope signatures is very high and makes

up the basis for very accurate use of this tracer – even within the Upper Cretaceous sedimentary column hosted formation waters. Strontium isotopes have been successfully tested to indicate contributions from Permian and Upper Cretaceous groundwater admixtures. Even within the mine water provinces, slight differences account for a fingerprint of mine waters from certain provinces. 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.

References

- Banner, J.L. (1995) Application of the trace element and isotopic geochemistry of strontium to studies of carbonate diagenesis. *Sedimentology* 42, 805–824.
- Burke, W.H., Denison, R.E., Hetherington, E.A., Koepnick, R.B., Nelson, H.F., Otto, J.B. (1982) Variation of seawater 87Sr/86Sr throughout Phanerozoic time. *Geology* 10: 516–519.
- Dugamin, E.J.M., Richard, A., Cathelineau, M., Boiron, M.C., Despinois, F., Brisset, A. (2021) Groundwater in sedimentary basins as potential lithium resource: A global prospective study. *Nature Scientific Reports* 11, 21091; doi:10.1038/s41598-021-99912-7.
- Hahne, C., Schmidt, R. (1982): Die Geologie des Niederrheinisch-Westfälischen Steinkohlengebietes – Einführung in das Steinkohlengebirge und seine Montangeologie. Verlag Glückauf, Essen, pp. 106.
- Henkel, L.; Melchers, C. (2017): Hydrochemical and isotopegeochemical evaluation of density stratification in mine water bodies of the Ruhr coalfield. In: Wolkersdorfer, C.; Sartz, L.; Sillanpää, M.; Häkkinen, A. (Eds.): Proceedings 13th International Mine Water Association Congress – Mine water & circular economy. Lappeenranta, 430-436



- Jasnowski-Peters, H. & Melchers, Chr. (2021): 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. International Mine Water Association Congress Proceedings, Wales 2021, 212-217.
- Jones CE, Jenkyns, HC, Coe AL, Hesselbo SP (1994) Strontium isotopic variations in Jurassic and Cretaceous seawater. *Geochimica et Cosmochimica Acta*, 58(14.): 3061-3074,
- McArthur, JM, Howarth, RJ, Bailey, TR (2001) Strontium Isotope Stratigraphy: LOWESS Version 3: Best Fit to the Marine Sr-Isotope Curve for 0–509 Ma and Accompanying Look-up Table for Deriving Numerical Age. *The Journal of Geology*, 109: 155-170.