Hydrogeochemical monitoring of mine waters for a controlled and sustainable mine water rebound – from a univariate to a multivariate tracer monitoring concept

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Abstract

The long-term mine water rebound associated with the former hard coal mining area in the Ruhr District, Germany, will be conducted in a controlled and sustainable manner to verify its containment and conformance. Mine water must not contaminate drinking water reservoirs for over 6 million inhabitants of the area with a 150 years long industrial heritage. Hence, a risk management concept and monitoring plan has been put in place to optimize this task. Recently, an integrated monitoring initiative by the District Council in collaboration with the operator RAG AG comprising gas, water and mining induced uplift topics has been installed and is currently working on defining the monitoring guidelines for the operator. This research on natural tracers contributes to the hydrogeochemical monitoring plan to identify mine water in the subsurface. The goal is to be able to monitor the extent of mine water migration in the subsurface. This task comprises benchmarking existing hydrogeological models and to evaluate mine water mixing with aquifers. Such aquifers comprise (a) the Cenomanian-Turonian regional aquifer at the base of the overburden section just above the coal-bearing Upper Carboniferous and (b) Upper Cretaceous formation waters, which are to some degree used economically by local industries and mineral water companies. During the past three years, multiple tracers comprising stable isotopes, trace elements and general hydrogeochemical parameters have been evaluated in a univariate manner to identify suitable natural tracer compounds. The evaluated tracers include the ion species ratio Cl-/Br-, the dissolved cations Li^+, B^+ as well as stable isotope geochemistry measurements (i.e. δD, δ18O,87Sr/86Sr). Br- and Li^+ qualify to best distinguish mine waters from aquifers in the region. The multivariate statistical approach to combine various natural tracers of mine water and aquifers is presented here to even distinguish separate mine water provinces and define the least possible infiltration ratio to detect mine water mixing with aquifers. Preliminary principal components analysis (PCA) results are presented in order to detect covariance within the current natural tracer mix and determine a suitable natural tracer combination to capture most of the data variance while enhancing the precision for fingerprinting mine water migration.

Keywords: Mine water rebound, Ruhr District, multivariate statistics, hydrogeochemistry, tracers

Introduction

Since the end of hard coal mining in 2018, the hydrogeochemical inventory of groundwaters associated with the mine water rebound in the Ruhr District, Western Germany, has been studied in order to determine suitable natural tracers for mine water. This work is a prerequisite to put a risk management and associated monitoring plan in place, which builds the legal and scientific foundation to be able to conduct the mine water rebound in a controlled and sustainable manner. Besides overcoming the restricted access to the former mine workings as well as reducing mine dewatering stations and combining mine water provinces for efficiency, major objectives for this research are (a) protection of drinking water reservoirs, (b) to avoid contamination of economically used groundwater reservoirs and (c) to take corrective action as soon as baseline thresholds were breached. During the past years, knowledge on the hydrochemistry of various aquifers, formation waters and mine water were gathered. Suitable candidates for tracking mine water and distinguishing it from aquifers and formation waters mimicking mine water, as it is the case for (a) the Cenomanian-Turonian regional saline aquifer immediately overlying coal-bearing Upper Carboniferous strata and (b) the sulfate and dissolved iron containing formation water of the Haltern Formation, have been evaluated. A suitable tracer compound need to be conservative, hence not changing due to physicochemical or biological processes, conventionally measurable down to a very low limit of detection (LOD), cost effective and in the best case contained in the natural inventory of common dissolved ions. Following natural tracers indicated a measurable difference of mine water vs. the existing groundwater inventory: (a) chloride to bromide mass concentration ratio (Cl^-/Br^-), (b) lithium mass concentration normalized to sodium mass concentration (Li^+/Na^+), (c) strontium isotopes (87Sr/86Sr), water isotopes (δD, δ18O) and to a lesser extent (d) boron mass concentration (B^+). Chloride to bromide ratio is a classical natural tracer to distinguish origin of salinity based on the early works of Rittenhouse (1967) and Rittenhouse et al. (1969). Molar concentrations of sodium and chloride were evaluated to further constrain the chloride to bromide trend. Strontium isotopes were measured with an accuracy down to 2σmean = 0.000005, which allows the ability to identify differences in adjacent water provinces. The reason for that is still evaluated, but links to the geological history of the region. In former benchmarking exercises and hydrochemical characterization of mine waters originated from hard coal mining in Europe (Gombert et al. 2017, 2019) bromide and lithium were not considered as the focus was on primary pollutants for water courses or groundwater. Hence, Gombert et al. (2017; 2019) focused on transition metals, chloride and minor ions like barium and strontium. However, boron as a classical tracer for organic matter accumulations like coal was considered. Boron concentrations ranged in the German coalfields from 0.23 mg/L to 13.0 mg/L. The natural tracers were evaluated after trying to find suitable differences in major ion distributions using Piper plots (Jasnowski-Peters & Melchers 2021). The sodium and chloride dominating mine waters, which often were buffered by bicarbonate, which was formed partly

in-situ by microbial processes, could not be distinguished with certainty from formation waters in the overburden section. The univariate screening for suitable natural tracers was finished with the outcome of five potential natural tracers, which qualify for risk management and monitoring purposes. To benchmark the five tracers and to try to combine those to optimize and better constrain mixing processes of mine water with groundwater from different origins, the next step in the scientific assessment of natural tracers is to go from a univariate to a multivariate statistical approach in combining those. However, a few tracers were acquired only recently together with general dissolved major and minor ion analyses like strontium and water isotopes. Hence, a suitable parent data population needed time to be gathered. From over 750 single mine and groundwater analysis, only a bracket of 20% could be tested to include all recently measured tracers except strontium isotopes. The aim of the multivariate statistical approach is to find a natural tracer set, which captures most of the variance of the dataset with the least possible numbers of tracers, i.e. principal components. Residuals determine a variance in the dataset, which is currently not captured with the evaluated tracers.

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-detection in order to be not influenced by high chloride concentrations. For further insights to the hydrochemical analyses, the reader is referred to previous publications (Jasnowski-Peters & Melchers 2021; 2023). Multivariate statistics were conducted using a MATLAB-based standard procedure. Scores and loadings were determined from a dataset of n = 166 with 13 variables containing major dissolved ions (Na, K, Ca, Mg, Cl), minor ions (Br, Li, B) the ratio Cl/Br, water isotopes (δD, δ^{18}O) and general parameters (depth, electrical conductivity). Data were pre-processed using an auto scaling routine. Plots shown are based on five principal components capturing 93.21% of variance.

Results

The multivariate statistical approach considered a number of variables as high as possible in order to adhere to the concept to "think as wide as possible". A necessary and mandatory outcome of the results should be if a variance in the dataset was missed out with the current set of variables. That would imply that an important natural tracer, which covers this variance, was not taken into account. The principal components analysis (PCA) approach lead to the following results:

Hence, choosing five principal components (PCs) captured 93.21% of the total variance in the dataset. In general, PCs < 0.5 Eigenvalue are not considered as a rule of thumb. The root mean squares error of calibration (RMSEC) for this approach is RMSEC = 0.260 and the root mean squares error of cross validation (RMSECV) is RMSECV = 1.174

Taking into account the most common major ions in this PCA leads to an evenly distributed loadings plot for 9 out of 13 variables with low to medium loading ratings of 0.27 to 0.33 in PC 1. The remaining four variables in PC 1 have loadings < 0.25. However, if you focus on PC 2, three of the four lower rated variables in PC 1 stick out. Boron (B) and chloride to bromide ratio (Cl/Br) indicate a positive correlation and have loadings > 0.5 with B = 0.58 and Cl/Br = 0.62. In PC 3 boron was considered to have the most prominent loading with B = 0.81 and is not correlated to any other variable. In PC 4, lithium got reasonably high loading with Li = 0.63, shows some correlation with calcium (Ca) and depth of sample taken (depth) and is anti-correlated with the water isotopes δ2H (dH2) and δ18O (d18O).

A bi-plot represents both, scores and loadings for the entire dataset and associated PCs. The bi-plot in Fig. 2 graphically represents PC 2 to PC 4 on the three axes. The loadings of the PCs which represent the variables lithium, boron, chloride to bromide and the water isotopes (δD, δ^{18}O) dH2 and d18O plot in three out of four quadrants. The samples AV 7 and M 8 can be considered "outliers" in the dataset, which was verified due to inconsistencies within the group of samples they belong to.

A first dendrogram was generated using cluster analysis. Based on Ward's method, the dendrogram was able to differentiate in parts mine water samples from different water provinces and clustered them reasonably well together. Fig. 3 shows two snapshots of parts of the dendrogram slightly overlapping.

Conclusions

A first approach of a multivariate statistical assessment using principal components analysis of a about 20% subset (n = 166) of the entire dataset (n = 748) verified to a high extent the previously conducted univariate natural tracer assessment studies. A natural tracer set consisting of boron, lithium, chloride to bromide mass concentrations (Cl/Br) and water isotopes (δ2H, δ^{18}O) indicated

***Table 1** Principal components analysis – Eigenvalues and variance captured*

Principal component (PC) Number	Eigenvalue of Cov(X)	% Variance captured This PC	% Variance captured Total
1	9.050	69.63	69.93
2	1.130	8.68	78.31
3	0.815	6.27	84.57
4	0.639	4.92	89.49
5	0.483	3.72	93.21

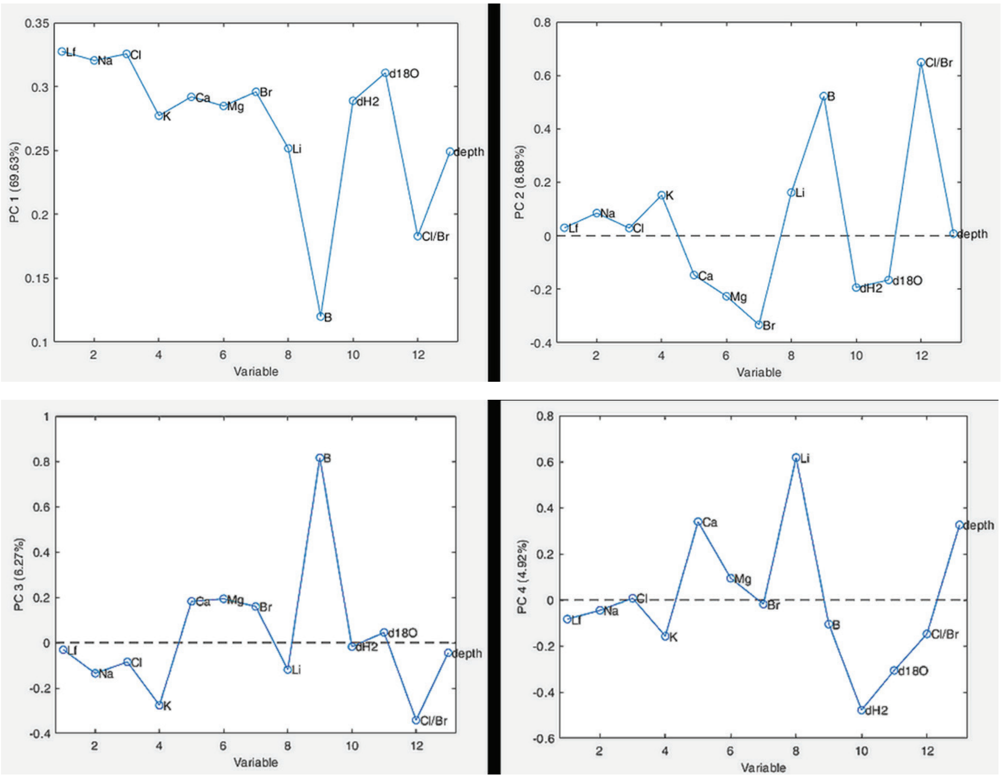

Figure 1 Loading's plots of principal components 1, 2 (upper row), 3 and 4 (lower row); dH2 and d18O indicate hydrogen and oxygen stable isotopes, i.e. water isotopes

loadings >0.5 and dominated PC 2 to 4. Hence, such natural tracers being part of PC 2 to 4 were able to represent enough of the variance of the dataset and to differentiate to some degree adjacent mine water provinces from similar Lower Carboniferous coal measures containing host rocks. The set of major ions showed no specific uniqueness and rather correlated to each other making them no usable natural tracer in a monitoring plan and risk assessment. Strontium isotopes as another prominent and promising natural tracer due to its accurate precision would improve the current PCA even further.

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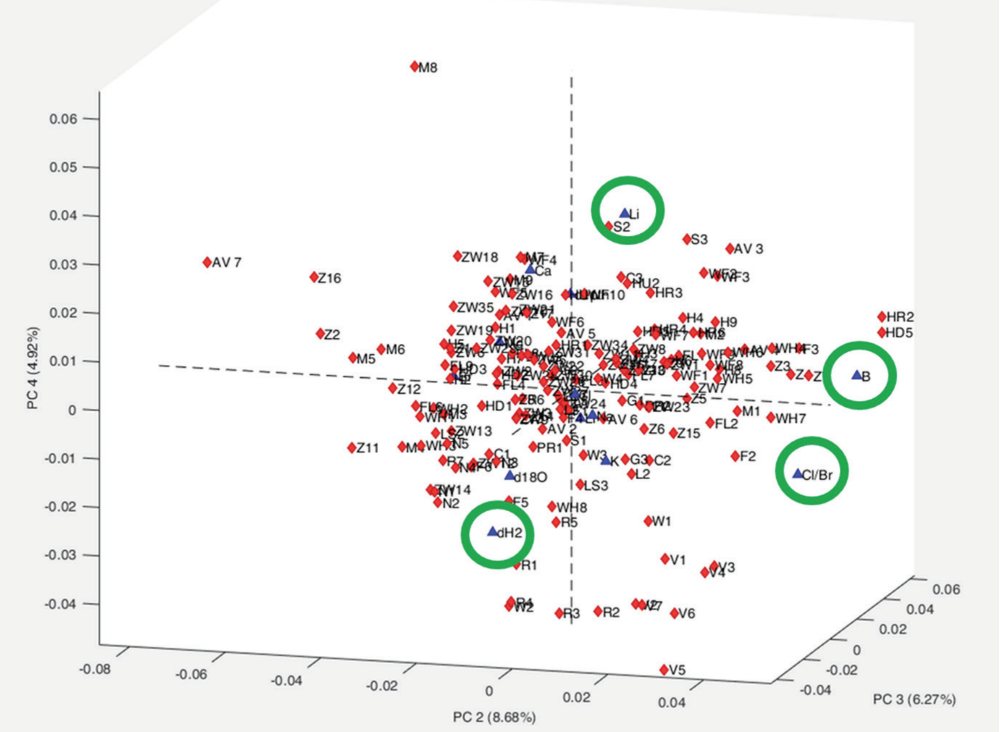

Figure 2 *Bi-plot graph of principal components 2-4; scores shown as red quadrangles, loadings shown as blue triangles; high loadings in the various PCs highlighted with green circles*

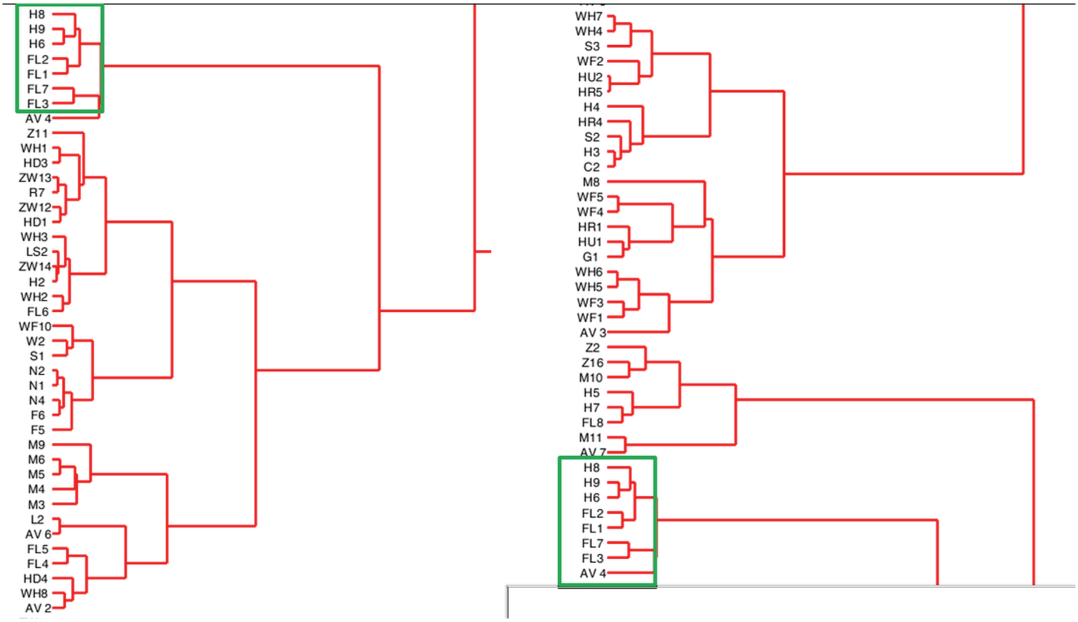

Figure 3 *Parts of a first dendrogram indicating good clustering of similar samples in a few clusters*

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