Hydrogeochemical Monitoring of Mine Waters for a controlled and sustainable Mine Water Rebound – from a univariate to a multivariate Tracer Monitoring Concept

Henning Jasnowski-Peters

Sebastian Westermann & Christian Melchers

Research Center of Post Mining

TH Georg Agricola Bochum

University of Applied Sciences

Monitoring concept outfit

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- **aim:** classification, distinguishing criteria, origin of salinity, regional hydrogeological system understanding
- current portfolio of natural tracers to evaluate the hydrogeochemistry of hard coal mine water in the Ruhr District
- tracking of mine water flow pathways in the subsurface/mine workings despite limited access
- hydrogeochemical data repository for all formation waters (incl. drinking water reservoirs), aquifers and mine water provinces
- **detection of mine water infiltration into aquifers during rebound is key**

Long term liabilities & integrated monitoring

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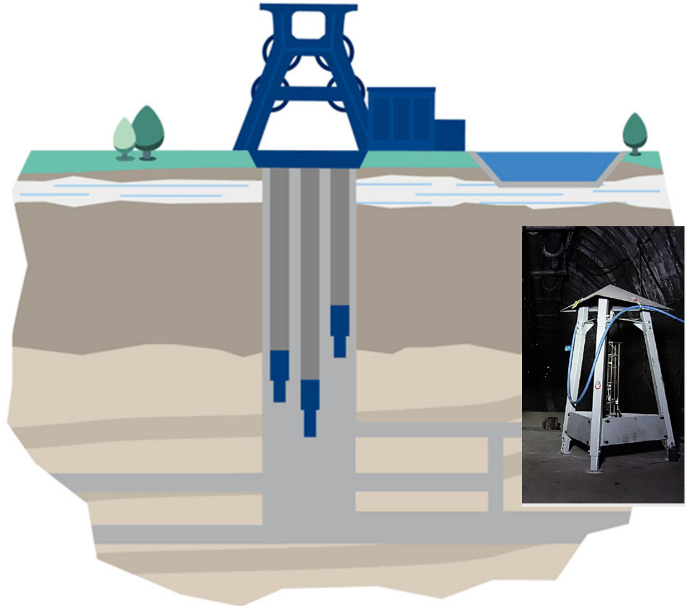
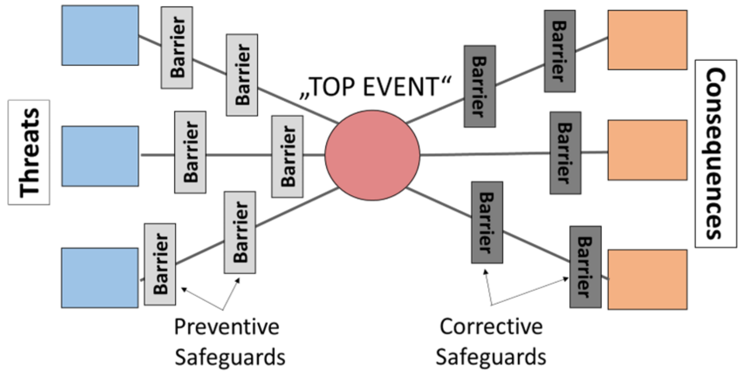
- perpetual obligations, i.e. long term liabilities, of RAG:
  - **Mine water management**
  - Polder measures
  - Groundwater/mine water discharge purification
- gamechanger project: **yearly costs ~300 Mill. EUR**;
- Risk management and integrated monitoring plan using „bow-tie“ method needs to be implemented.
- This research aims to deliver a hydrogeochemical toolset in order to verify containment of mine water.
- baselines for the various natural tracers (i.e. naturally occurring chemical species within the mine water) needs to be established

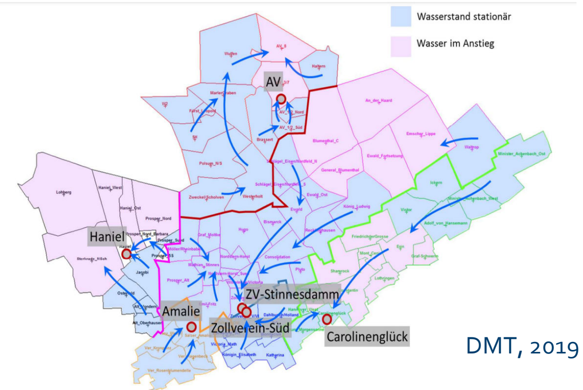




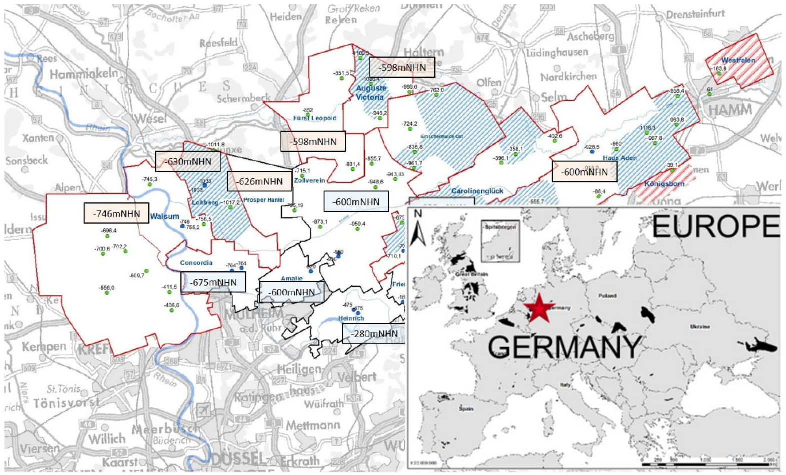
After Bourne et al. 2014

Mine Water Rebound in the Ruhr District

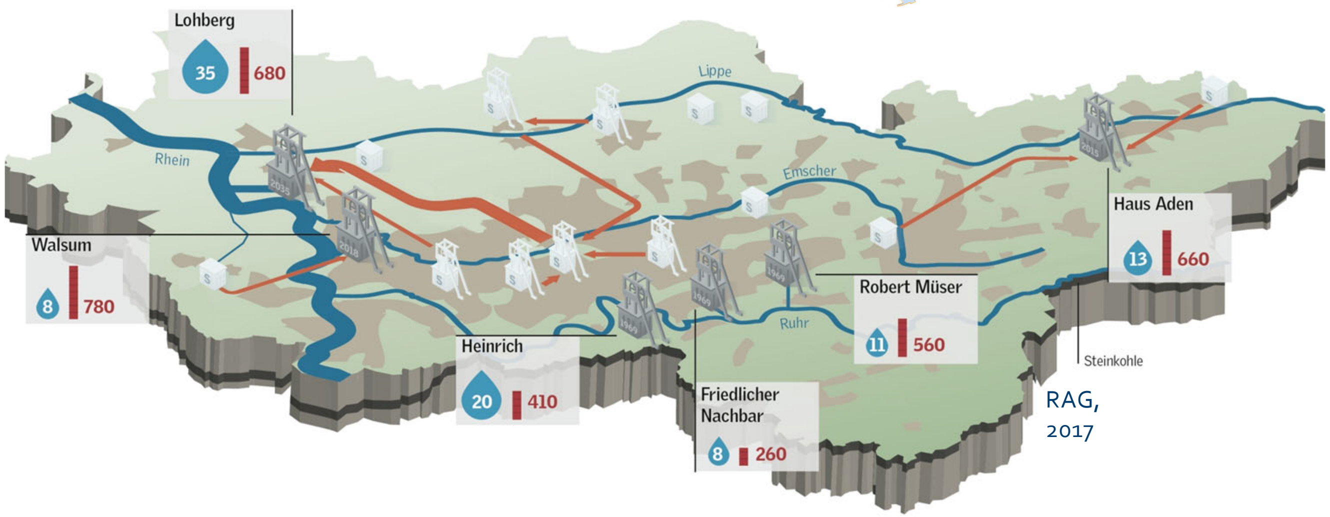
- Industrial hard coal mining in Germany ceased after 200 yrs at the end of 2018.
- Reduction of mine dewatering stations and keep river Emscher free of mine water discharge is pursued - approx. 65 Million m³ per year.



DMT, 2019



RAG, 2021



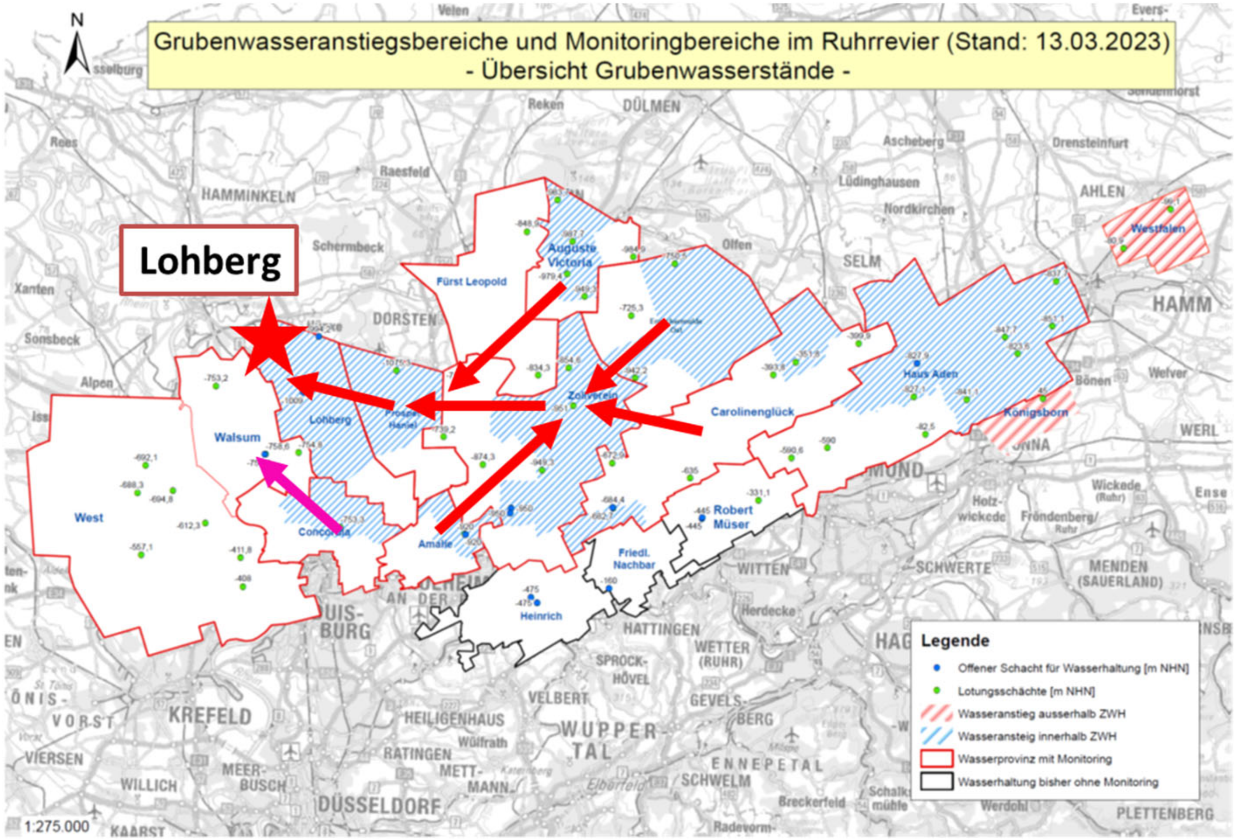
RAG, 2017

Current mine water situation

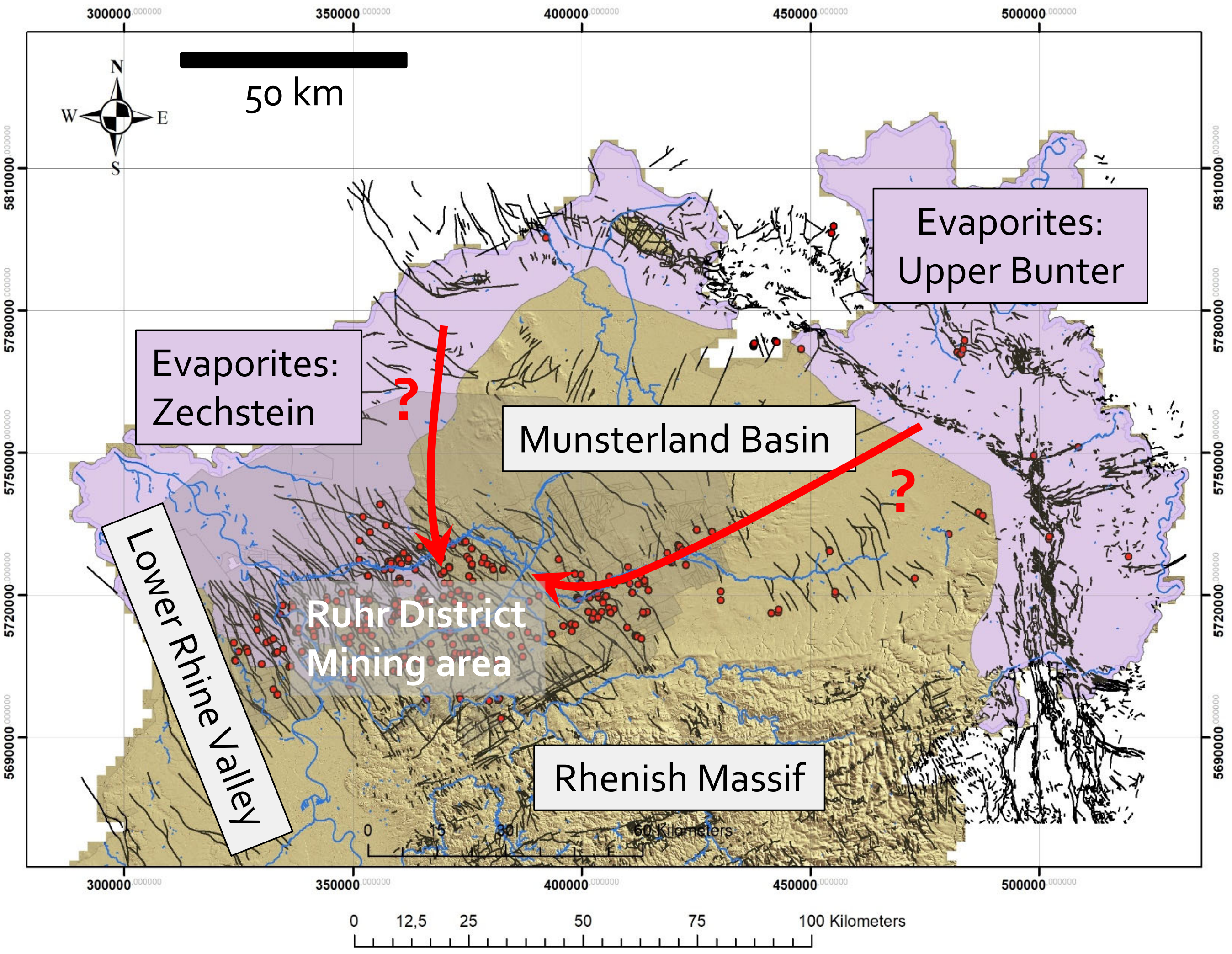
- mine water levels (03/2023):

LO	-1000m NHN
ZV	-950m NHN
AM	-900m NHN
CO	-750m NHN
WA	-750m NHN
HA	-830m NHN
CG	-680m NHN
HN	-475m NHN
FN	-150m NHN
RM	-445m NHN

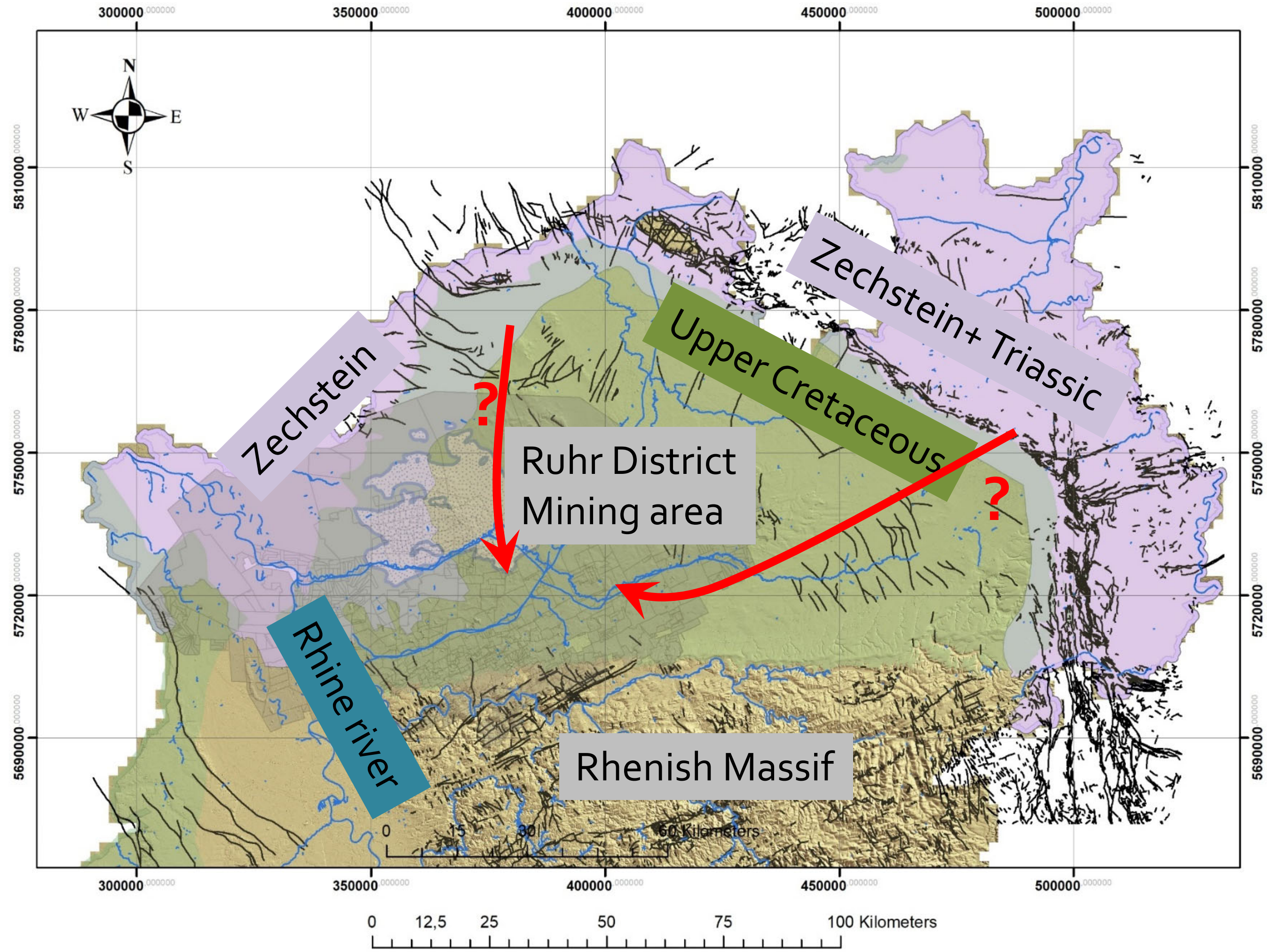
- focus on mine water flow from central part to Lohberg to discharge into the Rhine river (in 2030)



Hydrogeological system understanding



Hydrogeological system understanding – overburden strata



Hydrogeology: Cross section

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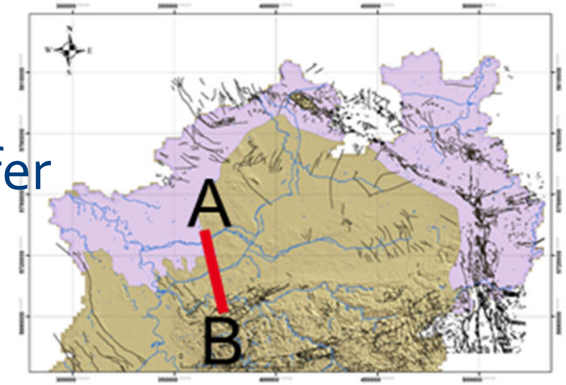
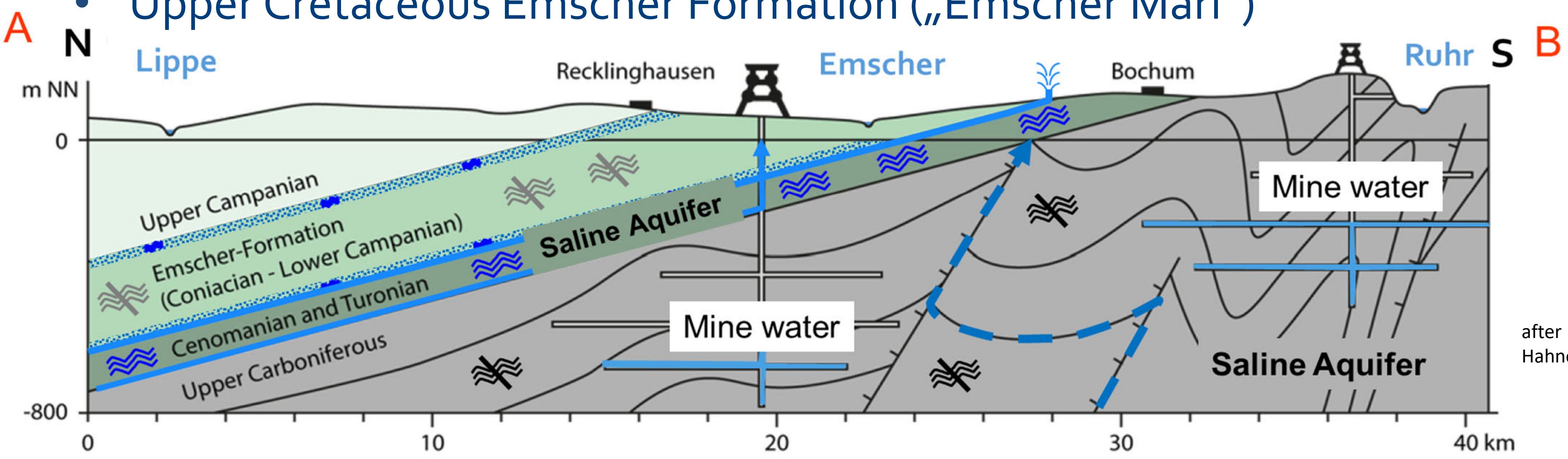
- **Two saline aquifers**
  - Upper Carboniferous formation water
  - Upper Cretaceous – regional Cenomanian Turonian aquifer
- **Two aquifers with sulfide oxidation (ARD)**
  - Upper Carboniferous mine water
  - Upper Cretaceous Emscher Formation („Emscher Marl")





after
Hahne & Schmidt (1982)

Hard coal mining related mine water in Europe – hydrogeochemsitry

- Gombert et al. 2017/2019
- Boron (B)!
- No bromide (Br)
- No lithium (Li)
- Samples: 600-800

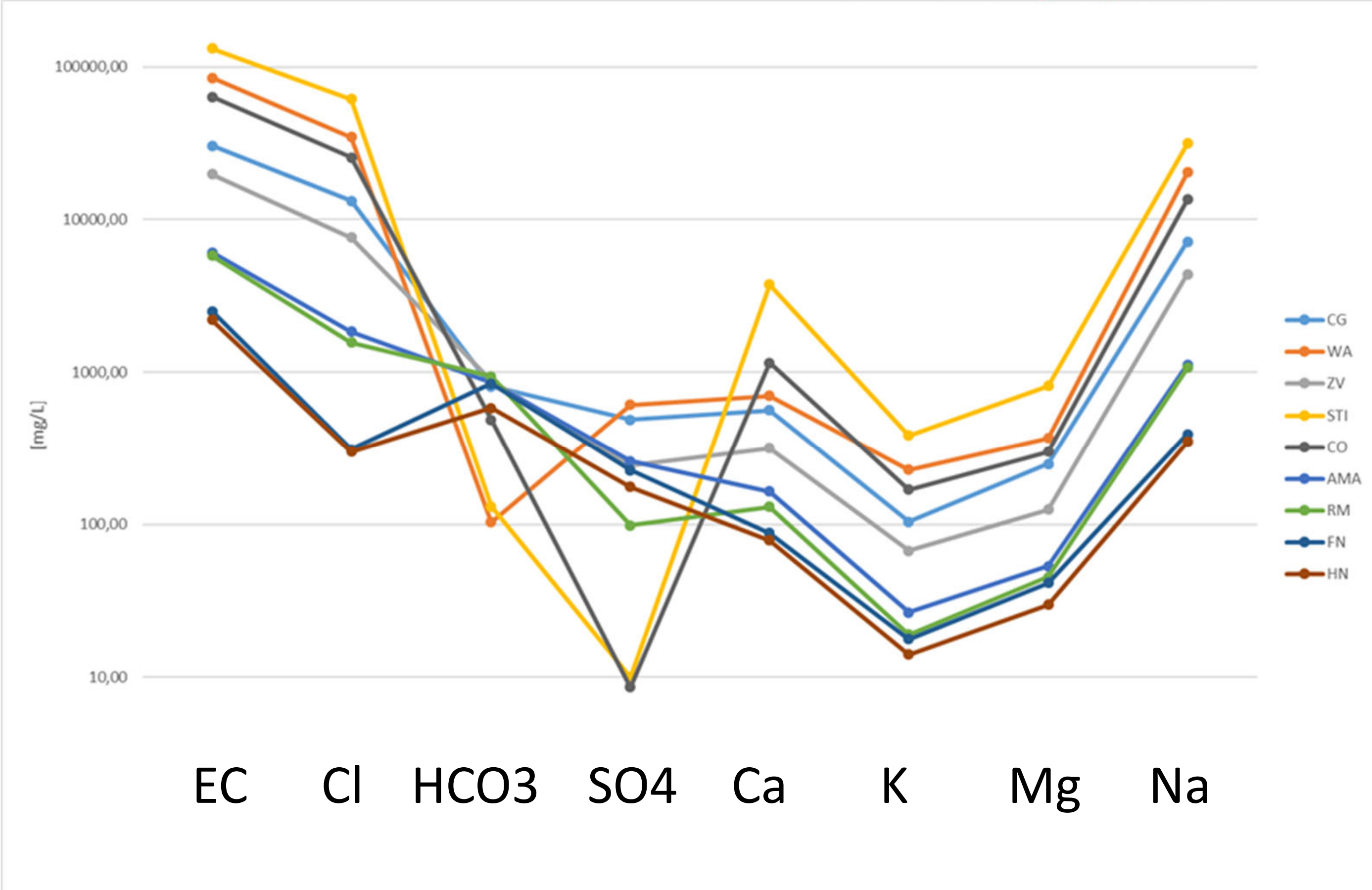
Table 2 Statistics of priority pollutants by country; Number (No.) represents the number of water samples analysed in the mines referenced in each country; "bdl" is below detection limit)

Country		Major ions (mg/L)				Minor ions (mg/L)				Trace elements (µg/L)								
		Ca	Mg	Cl	SO_4	Fe	Mn	B	Ba	As	Cd	Cr	Pb	Ni	Zn	Hg	Se	(Bq/L)
Greece	No.	60	60	60	60	60	60	0	0	60	60	60	60	60	60	60	10	0
	Min.	44	15	6	0	0.03	0.01			0.2	0.2	1.7	4.0	5.0	0.5	bdl	10.0	
	Max.	184	49	78	467	1.21	0.10			3.2	1.3	28.0	12.0	24.0	40.0	bdl	10.0	
	Ave.	94	28	16	144	0.18	0.03			1.1	1.0	3.9	5.1	8.7	6.8	bdl	10.0	
Spain	No.	67	67	0	65	65	63	40	0	40	40	40	40	40	0	40	20	0
	Min.	46	8		24	0.01	0.01	0.01		0.3	0.1	0.3	0.3	bdl		bdl	0.3	
	Max.	319	100		1747	9.05	0.92	0.19		9.4	0.1	0.6	4.8	2.9		bdl	0.4	
	Ave.	129	53		416	1.87	0.26	0.07		0.6	0.1	0.3	0.4	1.4		bdl	0.3	
Poland	No.	231	231	606	606	243	213	21	44	0	198	198	200	199	201	15	0	10
	Min.	1	21	41	119	0.01	0.01	2.23	0.12	bdl	bdl	0.6	0.4	0.3	0.3	0.1		0.060
	Max.	1062	707	36072	2868	39.0	8.27	4.25	7.70	bdl	130	155	560	421	17800	2.5		0.244
	Ave.	263	162	7579	783	3.59	1.30	3.19	5.06	bdl	9.3	18.9	60.8	43.3	287	2.3		0.160
United Kingdom	No.	1427	1378	1427	1225	1313	1427	1340	986	53	385	0	848	900	484	0	0	0
	Min.	1	1	6	3	bdl	0.03	0.01	0.01	1.0	0.3	bdl	1.0	10.0	5.0			
	Max.	1920	1180	29100	4680	91.5	77.0	7.36	0.06	900	2.6	bdl	2280	260	7840			
	Ave.	247	129	2296	944	34.2	5.58	0.73	0.03	21.9	7.3	bdl	85.5	53.1	40.4			
Germany	No.	601	601	795	792	758	650	571	604	41	557	522	531	531	572	104	0	81
	Min.	3	7	61	3	0.01	0.01	0.23	0.03	1.0	0.1	2.0	0.5	2.5	5.0	0.1		0.010
	Max.	5070	1320	101000	1890	330	28.0	13.0	580	10.0	40.0	130	1000	240	25000	0.6		7.30
	Ave.	841	291	12597	353	7.97	1.19	1.51	26.1	5.0	1.7	5.3	13.7	16.0	899	0.2		1.32
France	No.	84	82	84	100	99	94	5	3	51	29	26	23	28	31	17	0	0
	Min.	30	3	1	159	0.05	0.02	0.18	0.06	2.5	0.3	0.3	bdl	1.9	0.2	0.1		
	Max.	472	453	278	3010	43.8	9.11	1.01	0.11	347	25.0	57.2	50.0	32.0	500	1.0		
	Ave.	195	156	64	839	10.5	2.50	0.52	0.09	60.5	4.2	10.2	4.9	10.5	42.3	0.3		

bdl below detection limit

Mine water composition : Schoeller plots

- major cations and anions are not good distinguishing criteria
- deeper mine water – no sulfate
- bicarbonate buffered (pH 6.5-7.5), but no carbonates



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Univariate natural tracer evaluation

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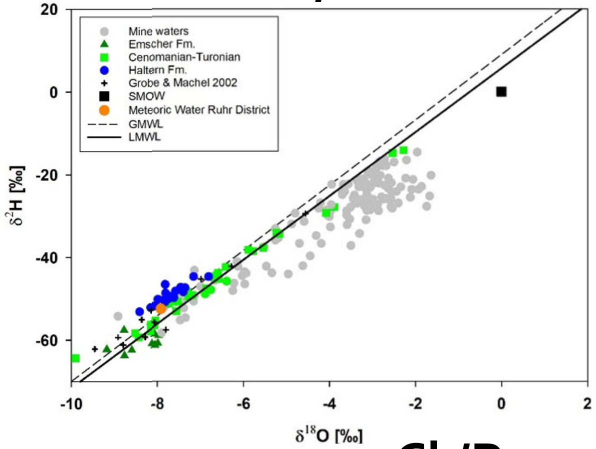
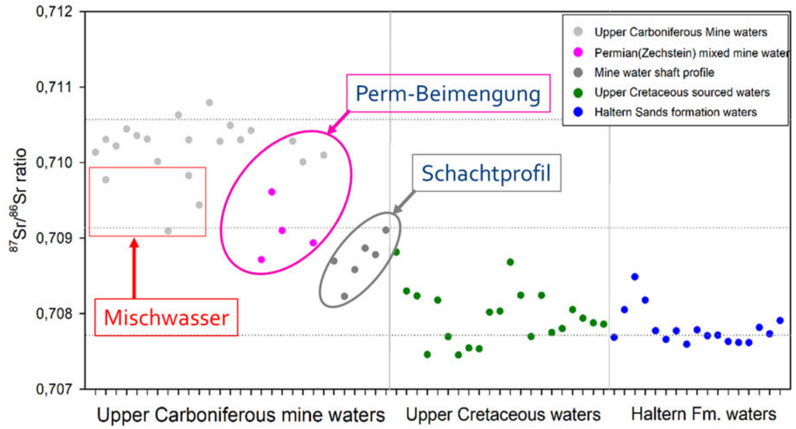
- $\delta^2H/\delta^{18}O$
- $^{87}Sr/^{86}Sr$
- Cl^-/Br^- [mg/mg]
- Na^+/Cl^- [mol/mol]
- Li^+/Na^+[mg/mg]

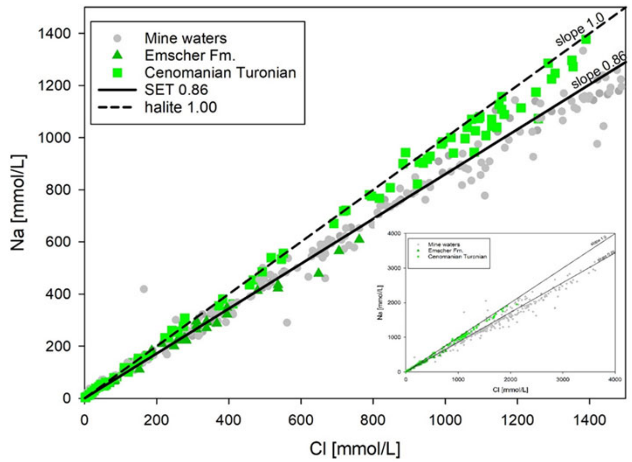
$\delta^2H/\delta^{18}O$



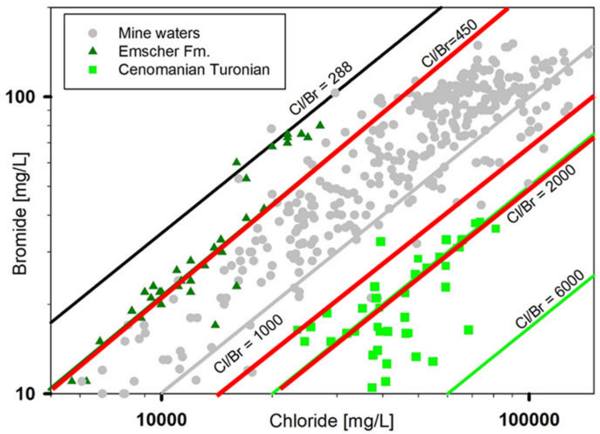
$^{87}Sr/^{86}Sr$



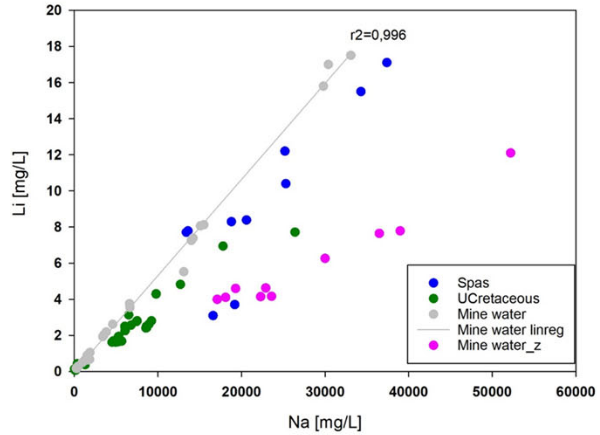
Na^+/Cl^-



Cl^-/Br^-



Li+/Na+



Mine water provinces
New water isotope data (2020-2023)

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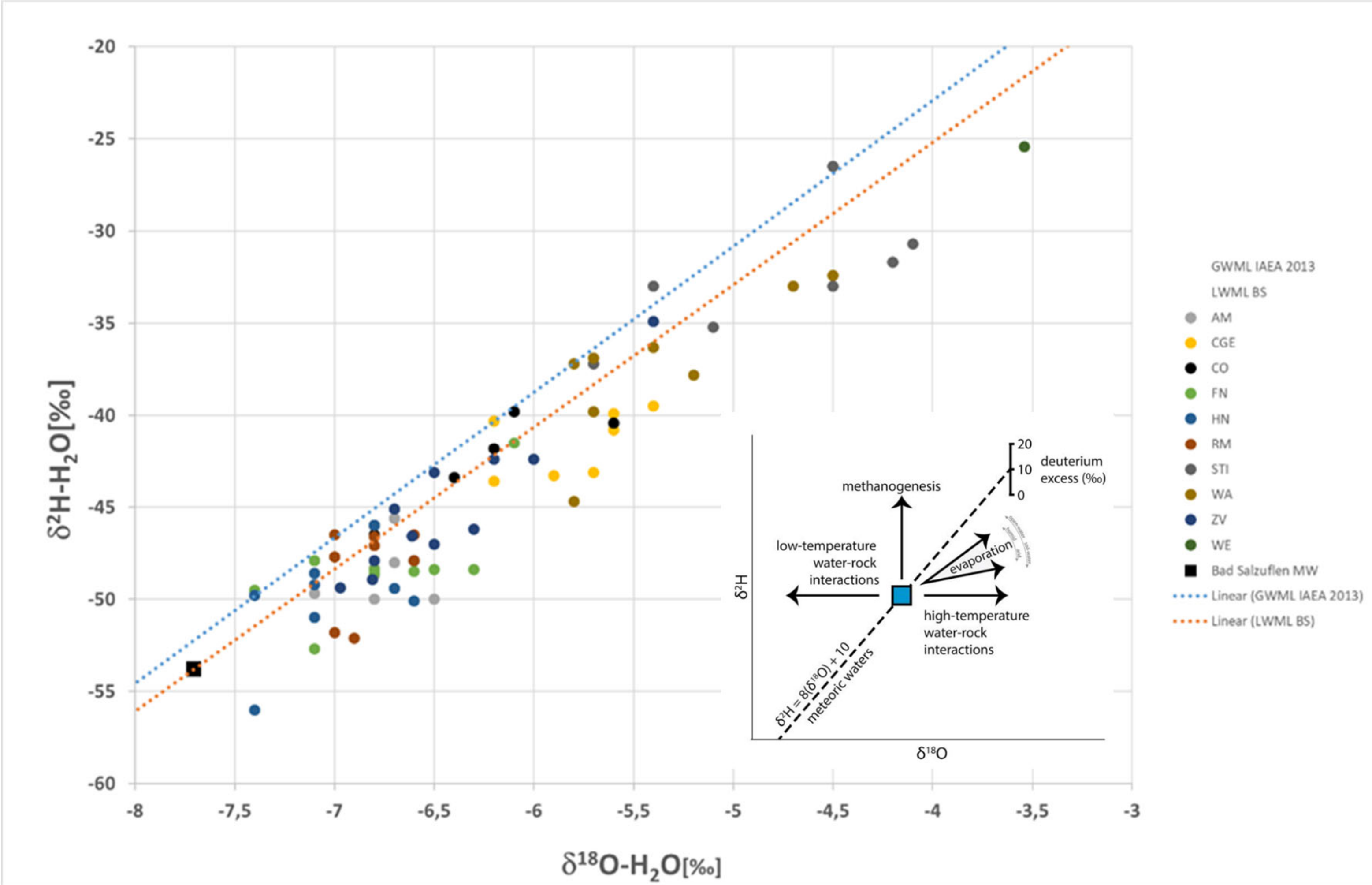
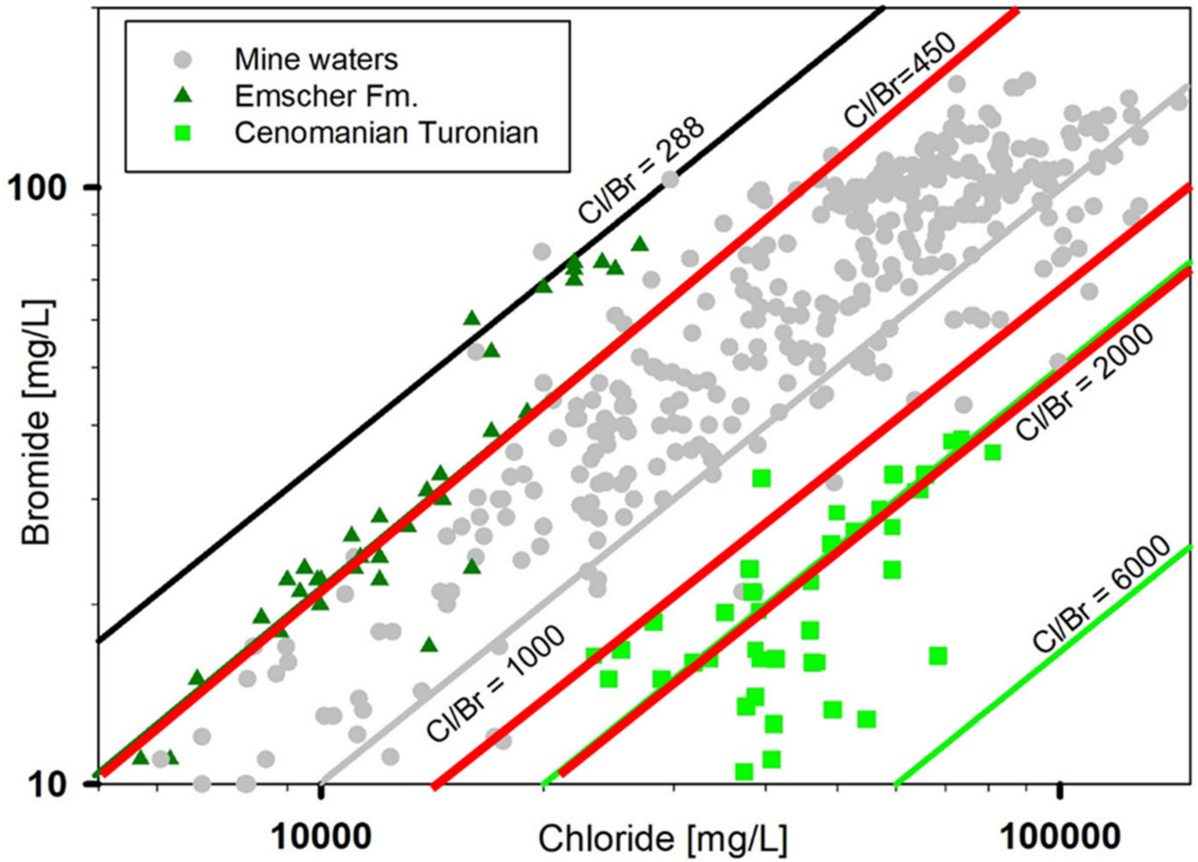
- recent water isotope data reveal water-rock interaction and evaporation pathways



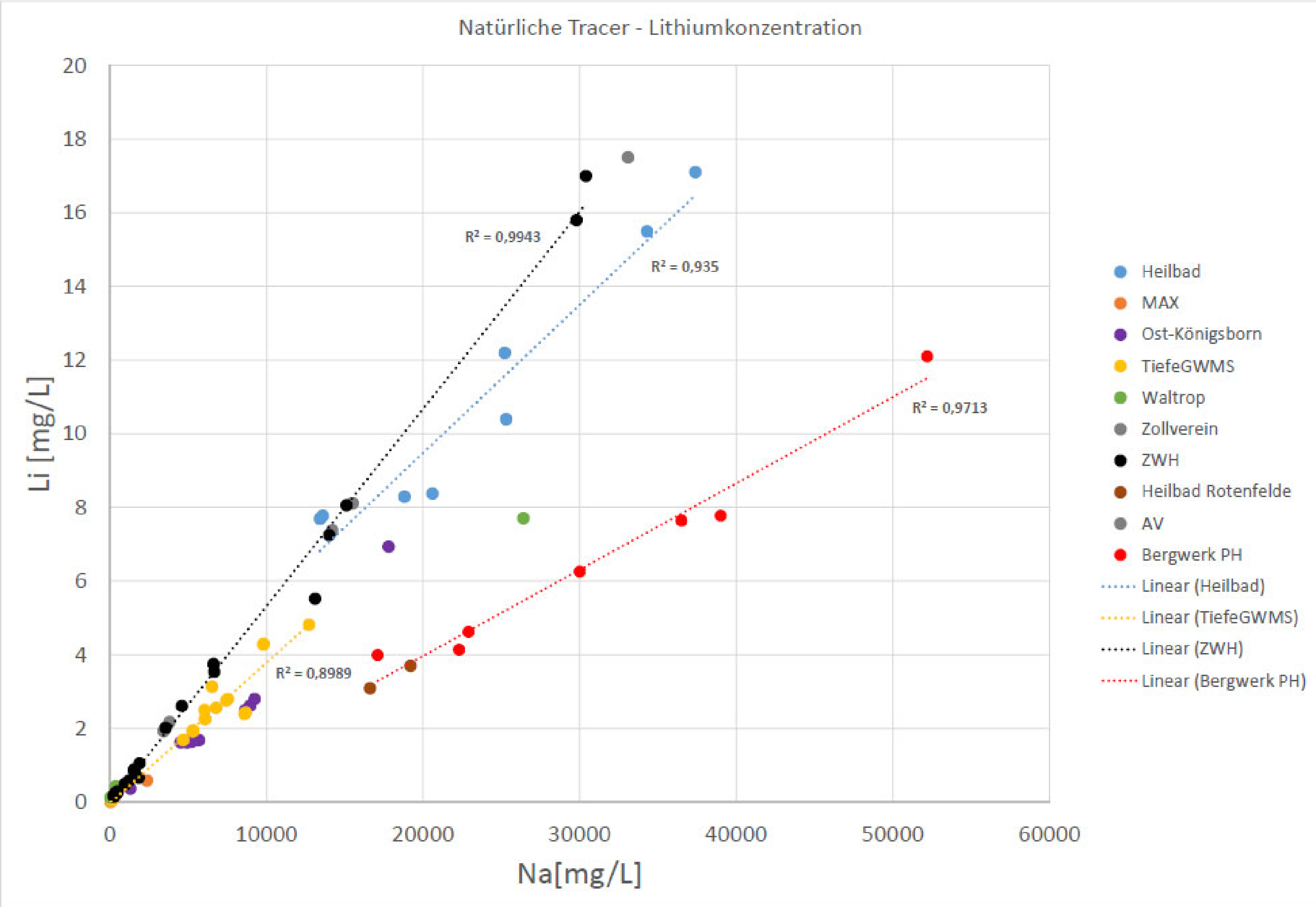
Tracer I: Chloride vs. Bromide

- Bromide as a natural tracer enables to distinguish mine waters from regional aquifers incl. formation waters of „Emscher-Formation" resembling mine waters and the saline aquifer „Cenomanian-Turonian" !
- **x<450**
  Emscher Fm. (kro)
  1450<x<450
  mine waters (c)
  x>1450
  Cenomanian-Turonian (kro)



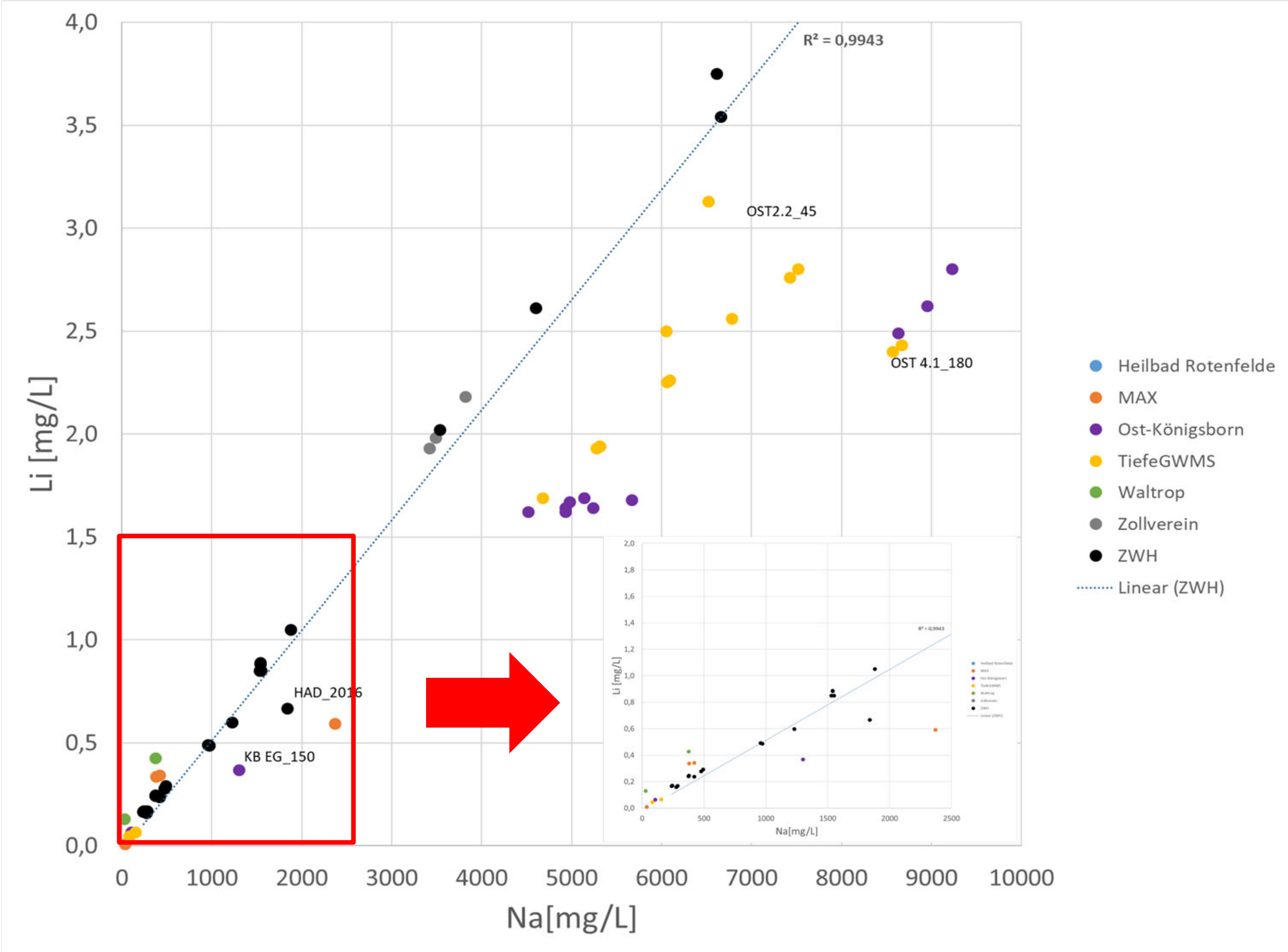
Univariate lithium tracer

- High R^2 correlation coefficient for mine water
- influence from Zechstein and Cretaceous overburden



Univariate lithium tracer: zoom-in

- Li natural tracer reveals high sensitivity using highres axial ICP-OES setup



Strontium isotopes $^{87}Sr/^{86}Sr$ – new highRes data

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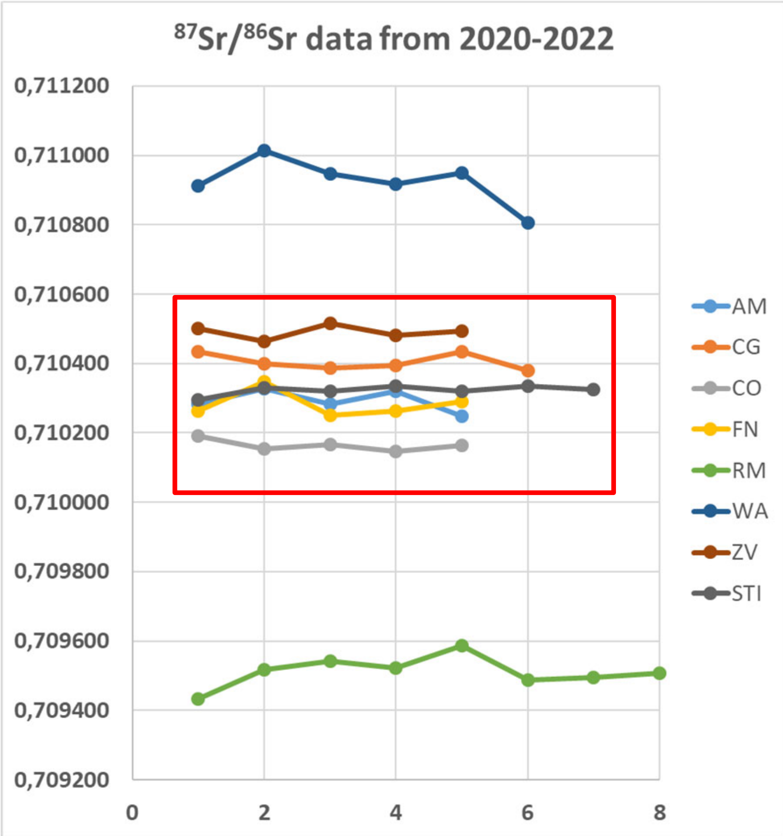
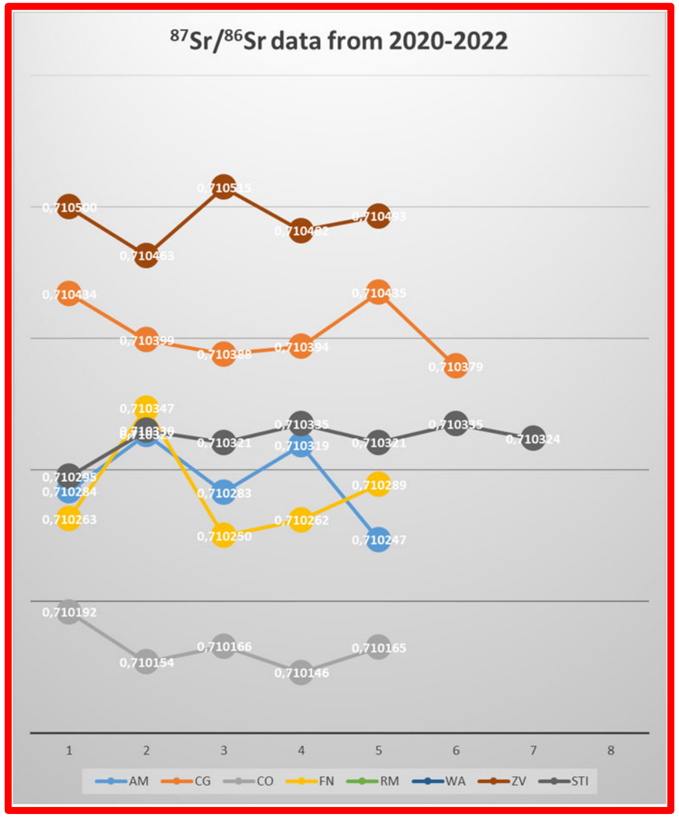
- $^{87}Sr/^{86}Sr$ isotope data from water provinces during time interval 2020-2022





Mine water provinces
Inorganic-organic exchange: DIC

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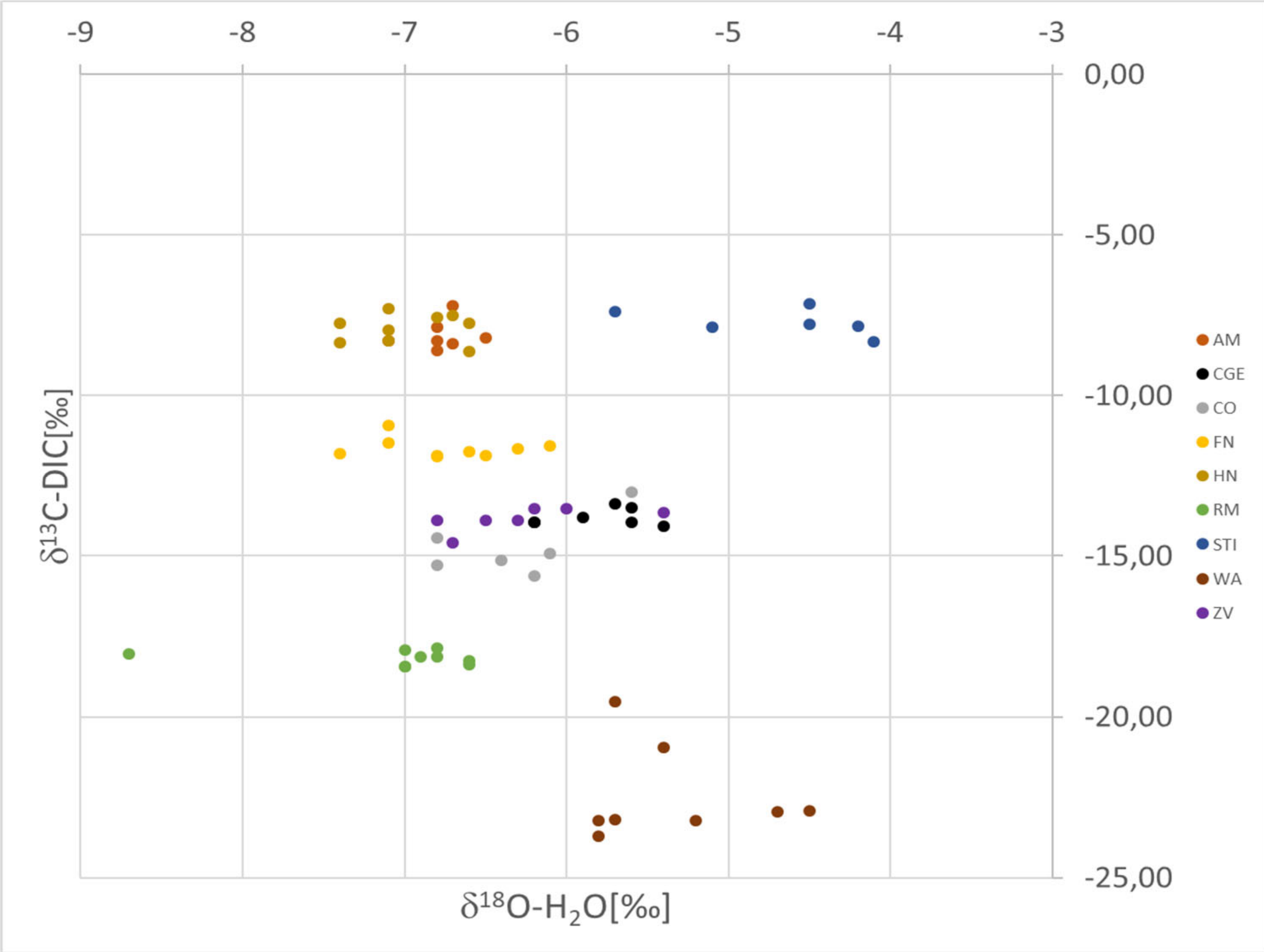
- $\delta^{13}C$ -DIC vs. $\delta^{18}O$-H_2O (2020-2023)
- stable $\delta^{13}C$ -DIC signal within the water provinces
- Good spread of $\delta^{13}C$ -DIC from -7 ‰ to -24.5 ‰



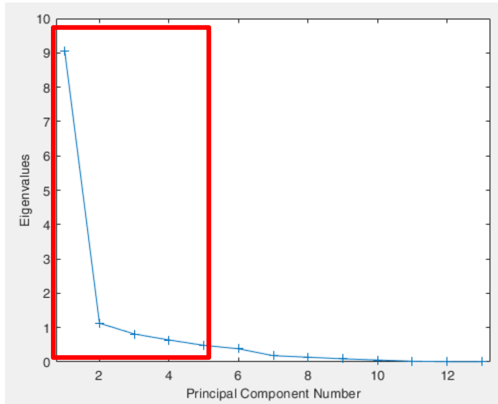
Multivariate analysis

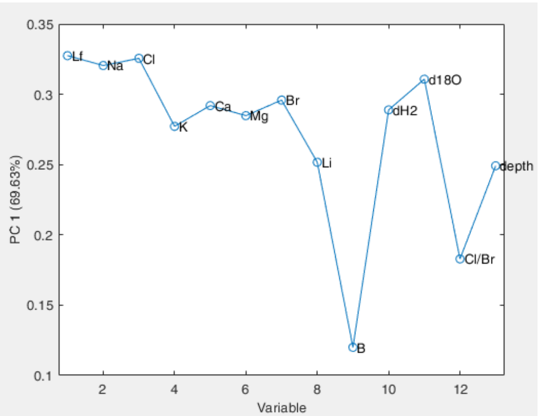
- Dataset:
  13 variables, 5 PCs
- 166 samples

RMSEC: 0.259832
RMSECV: 1.17401

Percent Variance Captured by PCA Model

Principal Component Number	Eigenvalue of Cov(X)	% Variance Captured This PC	% Variance Captured Total
1	9.05e+00	69.63	69.63
2	1.13e+00	8.68	78.31
3	8.15e-01	6.27	84.57
4	6.39e-01	4.92	89.49
5	4.83e-01	3.72	93.21





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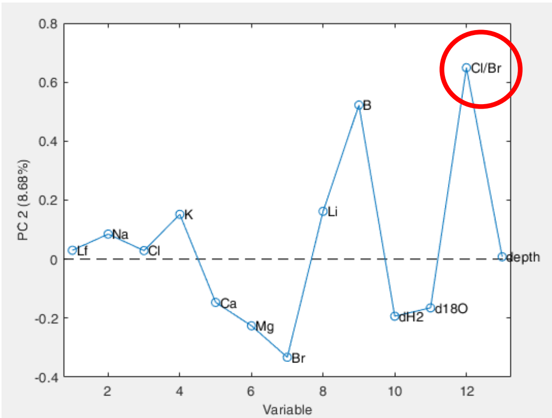

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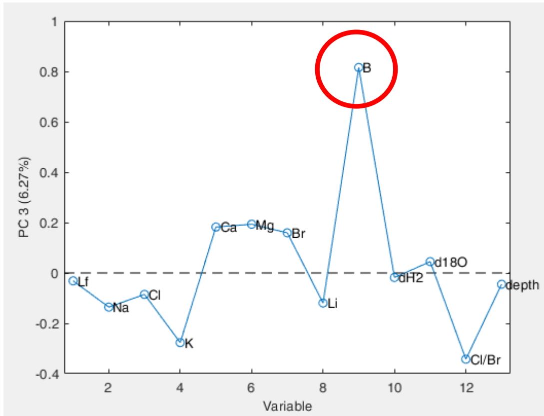

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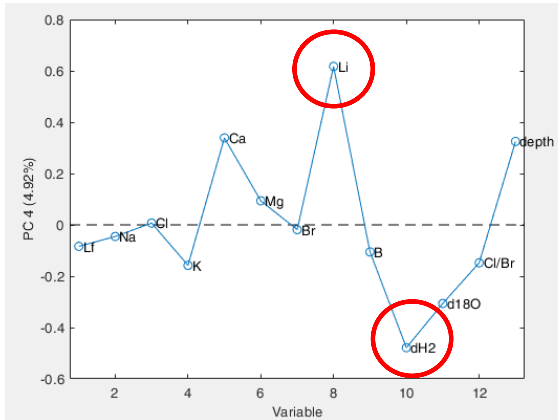

4

Multivariate analysis: Bi-Plot

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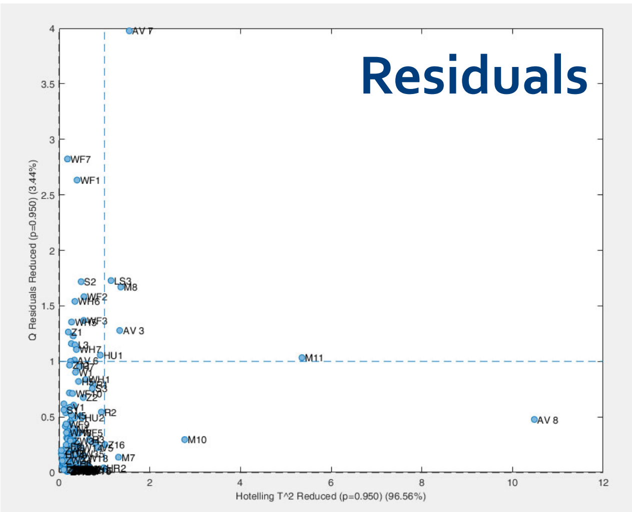
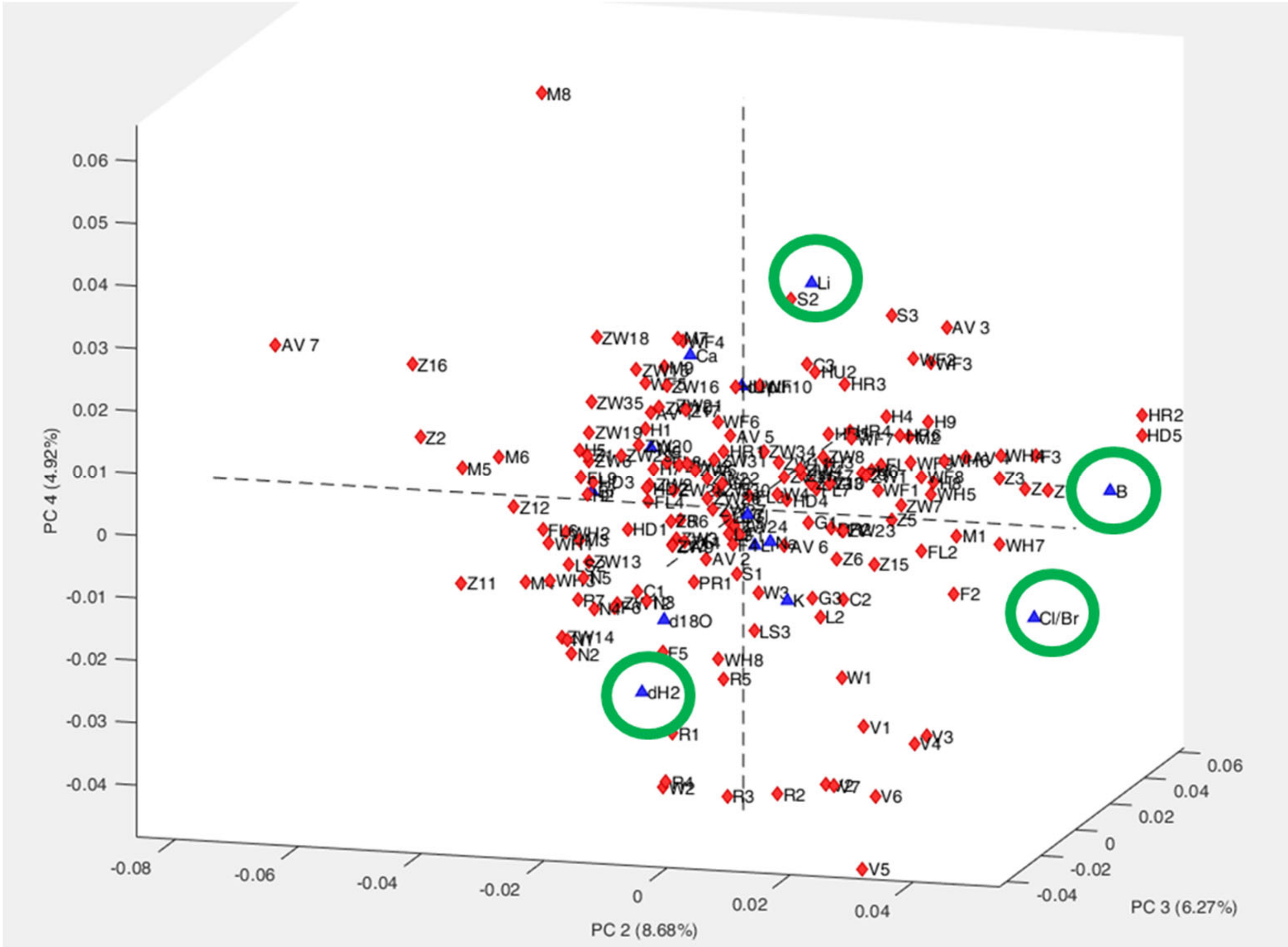
- PCs of Li, B, Cl/Br and $\delta^2H/\delta^{18}O$ are spread over many sectors





Cluster analysis: dendrogram

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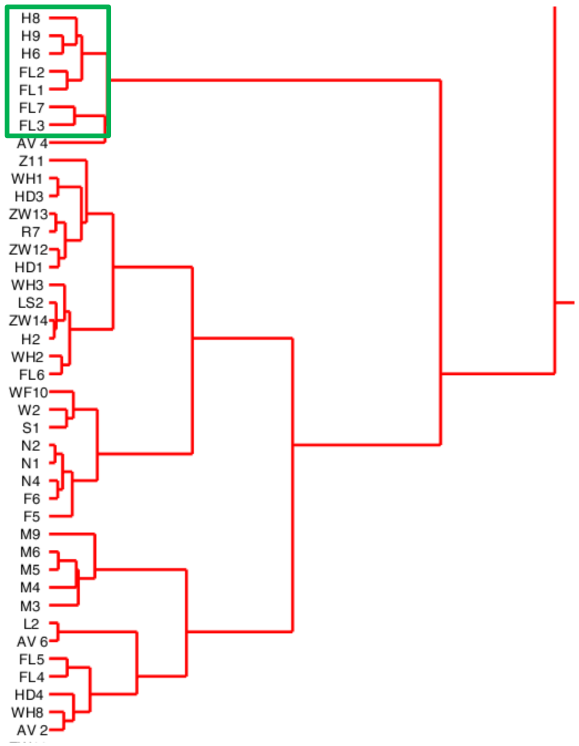
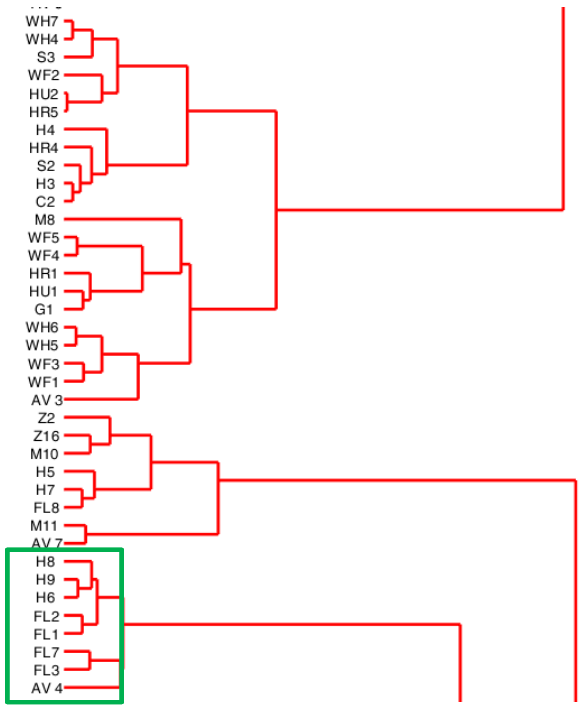
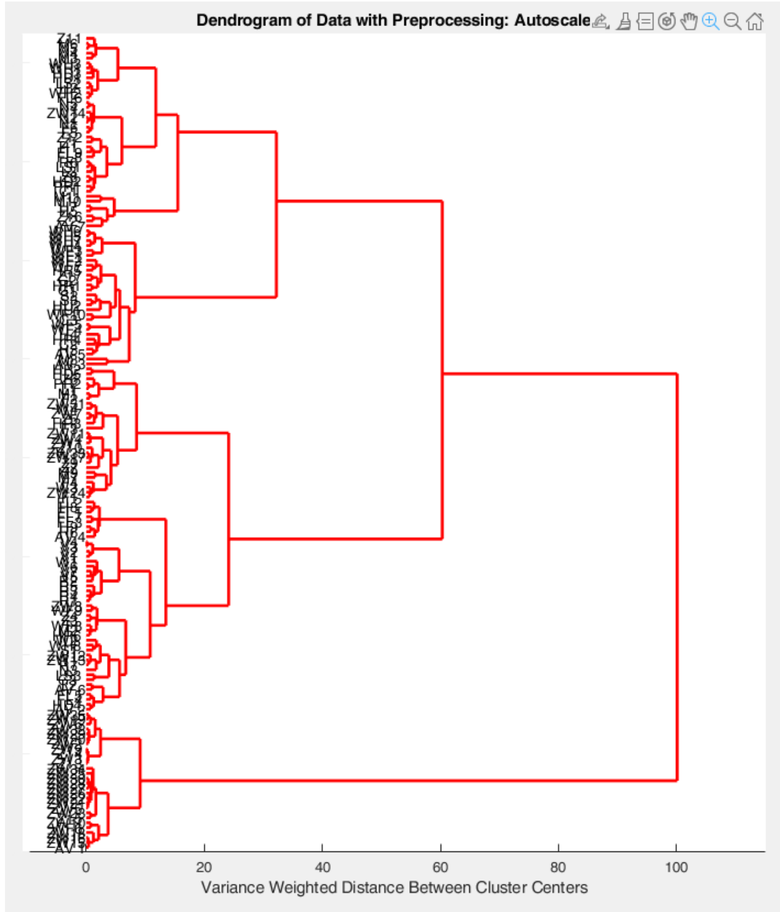
- on the basis of PCA results – Ward method







Conclusions

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- Natural tracers spanning over trace element cations and anions including stable isotopes have been presented which have the potential to distinguish and fingerprint mine water and formation waters/aquifers in the overburden section during rebound
- It is inevitable that this natural tracer mix can identify mine water and ist flow path; there is even a potential to distinguish certain mine water bodies, i.e. mine water from specific mine water provinces
- **the multivariate analysis** confirmed that the natural tracers which have been evaluated capture enough variance to identify mine waters
- Classification methods**(Clustering)** on the basis of the PC 2-5 indicated a fair grouping of similar mine water samples throughout a data matrix of n=166 spanning over the entire Ruhr District
- **Next step:**
  extending the data matrix and include the promising natural tracers of strontium isotopes, carbon isotopes of DIC and new water isotopes!!!!

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Thank you for your attention
and
Glückauf!

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