1000 Years of Mining: What Means Geogenic Background of Metals in the Rivers of the Harz Mountains?

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Abstract

Scope of the present study was a holistic approach to investigate the geochemically striking characteristics of the Harz Mountains in order to obtain reliable information about the respective metal concentrations in the overall Harz area. After World War II, the Iron Curtain split the Harz Mountains and since that time neither a common mine water management for the whole Harz Mountains nor a common assessment of the hydrological and hydrochemical data of the surface water monitoring systems of the neighbouring Federal States Saxony-Anhalt and Lower Saxony anymore existed. The present study is the first common assessment of the geogenic background since the Iron Curtain was established. The applied methodology makes use of defined percentiles of a statistically reliable database. The data base comprises a total of approximately 210 sampling locations with recent data after the year 1999, out of which remained after preselection 177 sampling locations. The key geochemically striking elements due to naturally increased metal concentrations in the metallogenic riverine landscape are Al, As, Be, Cd, Co, Fe, Mn, Ni, Pb and Zn in the East Harz as well as Ag, Hg and Pb in the West Harz. Due to the results, the Harz Mountains will be subject to WFD exemptions.

Key words: Natural background level of mining or metallogenic landscapes, Harz Mountains

1. Introduction

With the implementation of the EC Water Framework Directive 2000/60/EC (WFD) [1] and its key objective of a holistic water management at the level of river basins also mining areas are in the focus due to certain geochemically striking characteristics. The objective of the WFD to reach a high level of protection of the aquatic environment, reflected by a good chemical and ecological status by 2015, may not be reached in riverine landscapes with metallogenic origin. However, the WFD provides a number of exemptions that allow for less stringent objectives, including the extension of the implementation deadline maximum by 2027. Such criteria are

1. the technical feasibility is not given within the timeline
2. disproportional increase of costs when completing the measures within the timescale
3. natural conditions do not allow to achieve an improvement of the water body status timely.

Regarding to the last point, natural conditions may include elevated geogenic metal concentrations caused by natural specific local conditions leading to concentrations in surface water, which are not in conformity with the Environmental Quality Standards (EQS) of Directive 2008/105/EC [2]. To determine less stringent objectives for the implementation of the WFD due to naturally elevated geogenic metal concentration, an assessment about the geogenic background concentration in surface waters is necessary. Geogenic background concentrations are defined as concentrations, which naturally occur in surface water without any anthropogenic influences.

The objective of the present study was a holistic approach to investigate the geochemically striking characteristics of the Harz Mountains in order to obtain reliable information about the respective metal concentrations in the surface water of the overall Harz area. The data will be used as a justified and reliable basis for the application of exemptions according to WFD article 4 and the respective EQS according to Directive 2008/105/EC.

2. Geological Setting and Mining Activities in the Harz Area

2.1 Geology of the Harz Mountains

The Harz Mountains were formed during the Variscan orogeny 300 Mio. years ago by folding, uplifting and erosion. The Harz Mountains consist of Paleozoic rocks, mainly Devonian and Carboniferous rock formations. A smaller stripe of the western and southern Harz Mountains consists of Rotliegend and Zechstein as well as Silurian in the Lower Harz. Especially in the Central Harz, around the Brocken area, but also spread over the whole Harz Mountains, there is volcanic rock. Due to a strong diagenetic hardening at metamorphose conditions the rocks are solid without a mentionable permeability.

Geologically and morphologically the Harz Mountains can be separated in three areas (the Upper Harz, Central Harz and Lower Harz), which differ in their geological settings and the magmatic, tectonic, sedimentary and erosional genesis. The Upper Harz is geologically dominated by the Clausthal Culm Fold Belt, the Upper Harz Devonian Saddle and the Acker Bruchberg Zone. The Upper Harz comprises the Oker Granite, the Ecker Gneiss Complex, the Harzburg Gabbronorit Massive, as well as Diabas in the western part of the Brocken Granite. The north western part of the Central Harz is formed by the Blankenburg Fold Belt, including the Elbingeröde Complex, the Tanner Greywacke and the Sieber Depression. The Central Harz consists of Carboniferous intrusions, Devonian schists, Diabas, greywacke and granite (eastern part of the Brocken, Ramberg). The Lower Harz includes the Harzgerode Fold Belt with the Selke und South Harz Depression as well as the Wippra. It is formed by Ordovician and Devonian greywacke formations and molasses basins of the lower Permian ([3], [4], [5]).

All three geological units of the Harz Mountains show the occurrence of vein deposits with different mineralogical characteristics (see figure 2). The ore veins have been formed during the younger tectonic expansion. As a result of multiphase fault tectonic events there exists a system, which typically have an arch shaped course, leads to a crosslinking of all important veins [6]. In the Upper Harz (mining areas amongst others Clausthal-Zellerfeld, Grund-Silbernaal, Lautenthal) Middle and Upper Devonian layer bound lead-zinc-barytes and iron ore deposits have a great significance as well as Mesozoic lead-zinc-mineralisations. In the Central Harz silver-antimony-sulphosalts are of importance. In the south and southwest there are quartz-magnetite-chalcopyrite veins, quartz-hematite veins baryte-hematite veins and baryte-veins. In the Lower Harz there are imports deposits of pyrite, siderite and flourite. Lead-zinc-ores are not as significant as in the Upper Harz [5].

2.2 Mining Activities

The origins of mining in the Harz Mountains date back nearly 1000 years. In the middle age the mining in the Harz Mountains reached a prospering period. Main products of the mining activities were silver, copper, lead and iron and since the 19th century also zinc. From the 16th to the 19th century about 40 to 50 % of the silver produced in Germany had been mined in the Harz Mountains. In the 20th century the mining activities in the Harz Mountains decreased. In 2007 the last mine closed in Bad Lauterberg.

From the middle age until the early 20th century the miners created a huge network of facilities for the production of waterpower and the water management, the so-called "Oberharzer Wasserregal". It consists of at least 143 water-retention basins, more than 500 km ditches and 30 km underground watercourses. The facilities are spread over 200 km² in the western part of the Harz Mountains. Also in the Lower Harz exists a system of ponds and ditches for the water management in the mining areas. However, it does not have the extensions as the system in the western Harz.

2.3 Hydrology

The Harz Mountains form a watershed between the Elbe catchment area in the east and the Weser catchment area in the west. The rivers which drain in the west are the Oker, Oder, Sieber, Söse, Innerste and Weser itself. The rivers which drain in the east are the Wipper, Selke, Helme and Bode with

Rappbode. The subordinated catchments areas and their numbers of water bodies are listed in table 1. Figure 1 shows the spatial location of the catchment areas.

Table 1 *Catchment areas and number of water bodies (in brackets: number of investigated water bodies when different from total number)*

Elbe Basin		Weser Basin			
River	waterbodies	River	waterbodies	River	waterbodies
Wipper	4 (2)	Oker	11	Söse	7
Selke	4 (3)	Oder	9	Innerste	12
Helme	4 (2)	Sieber	7	Weser	2
Bode + Rappbode	16 (14)				

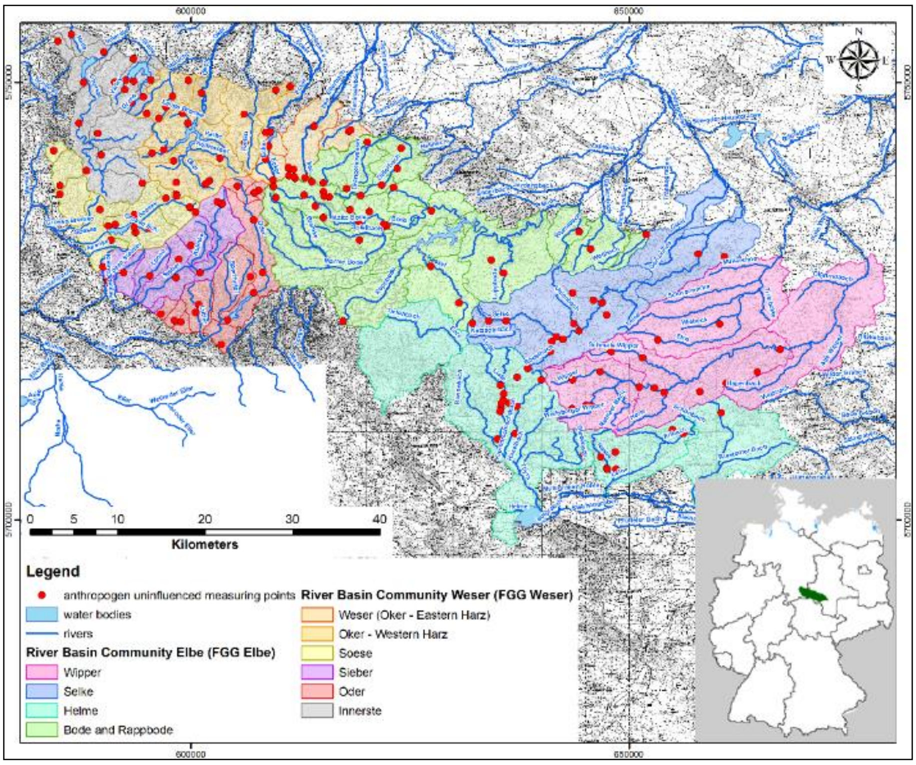

Figure 1: *Overview map of the river basin communities (FGG), the catchment areas in the Harz Mountains and the anthropgenic uninfluenced measuring locations.*

After the classification according to Briem [7] the riverine landscapes of the Harz Mountains are dominated by the metallogenic typ. Smaller parts especially around the Brocken are described as siliceous. Carbonatic-dolomitic landscapes are of minor importance.

3. Methods and Materials

In the EU there is not yet a generally accepted and standardized methodology to assess the geogenic background concentration in surface water. The total concentration of heavy metals in a river is the sum of a complex combination of natural and anthropogenic factors. The applied approach was developed by Schneider et. al. (2003 [8], 2014 [9], and 2016 [10]), the authors adapted and upgraded a general methodology for natural background concentration in groundwater developed by Schleyer & Kerndorff (1992) [11]. The methodology makes use of defined percentiles of a statistically reliable database, which includes metal concentrations of the total phase and the dissolved phase. The data were obtained from the monitoring network of the competent authorities of Saxony-Anhalt (State Authority for Flood Protection and Water Management Saxony-Anhalt) and Lower Saxony (Lower Saxony Water Management, Coastal Defence and Nature Conservation Agency) complemented by additional measurements to close gaps in the existing data base. The procedure was validated through the data of Birke et. al. (2006) [12] and comprises following steps:

- Elimination of all sampling locations from the database which have anthropogenic influence due to point sources (preselection of sampling locations). This applies to sampling locations, in whose catchment areas mining activities, like mines, mining piles, smelters or the Oberharzer Wasserregal are identified (based on date of fig. 2) and also contaminated sites, settlements and industry.
- GIS-based allocation of the sampling points with respect to the catchments areas, being the evaluation units,
- Elimination of the diffuse anthropogenic inputs which were defined as the concentrations larger than the calculated 90% percentile (P(90)).
- Assessment of the geogenic background by statistical calculation of the 90% percentile (P(90)) of the preselected data to find out the anthropogenic uninfluenced concentrations per surface water body.

For the measured data for the eastern Harz the first step was omitted, since already preselected data without anthropogenic influences were provided by the State authority for flood protection and water management Saxony-Anhalt (LHW).

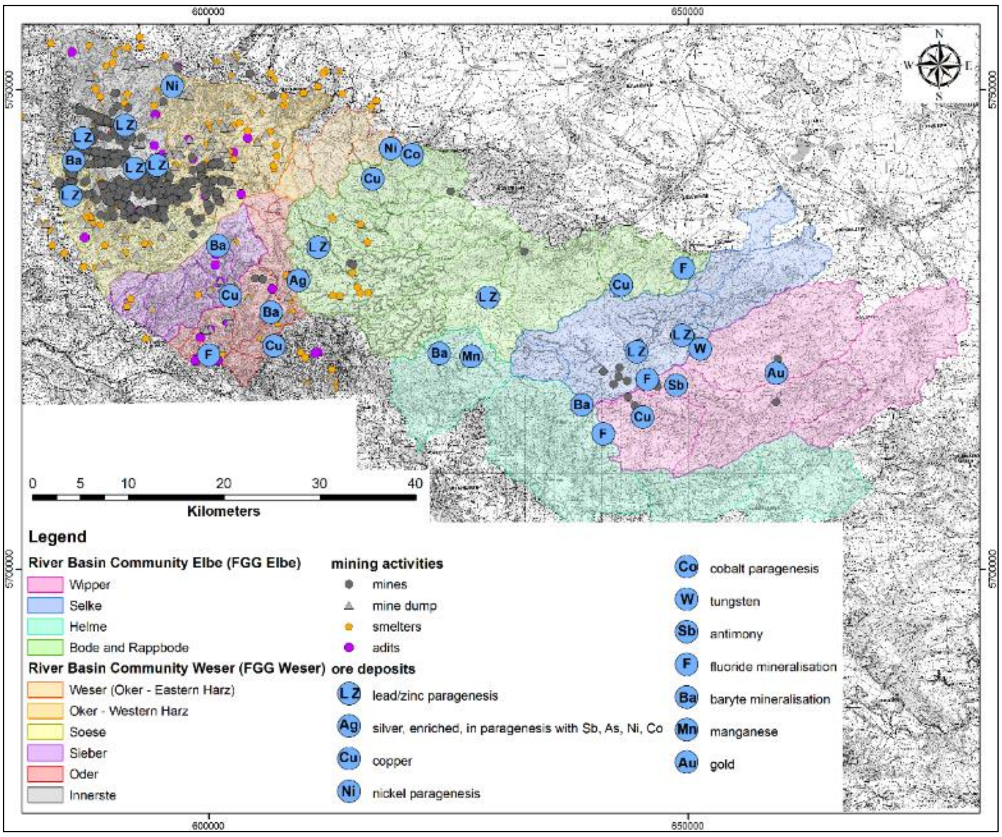

Figure 2: *Overview map with ore metal ore deposits and mining activities in the Harz Mountains.*

4. Results

Figure 1 shows the remaining sampling locations in the Harz Mountains after the method from chapter 3 was applied. Based on these sampling locations and their data, the results were calculated in the following tables.

The calculated geogenic background concentrations for the total phase are presented in table 2 and for the dissolved phase in table 3. For the total phase, only for three elements an EQS is defined. For silver, in all catchments areas of the western Harz the background concentrations exceeds the EQS, but for no catchment area in the eastern Harz. This is accordance with the western Harz as a significant mining area for silver. The other two elements, for which an EQS for the total phase is defined are selenium and thallium, however both are of minor importance in the Harz region, and there is no exceeding of the EQS for both.

Table 2: *Selected geogenic background concentrations of the total phase in the catchment areas of the Harz Mountains, calculated as the arithmetic mean of the 90%-percentile of the single water bodies, and EQS-values (**bold**: concentrations > EQS).*

	Unit	EQS	Oker P90	Oder P90	Sieber P90	Söse P90	Innerste P90	Wipper P90	Selke P90	Helme P90	Bode P90	Weser P90
$\mathbf{Ag}_{tot}$	µg/l	0,02	**0,92**	**0,25**	**0,24**	**0,27**	**0,32**	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
$\mathbf{Al}_{tot}$	µg/l		782	693	323	607	651	n.a.	n.a.	< 10	445	290
$\mathbf{As}_{tot}$	µg/l		1,16	0,75	0,25	0,63	0,25	4,54	1,69	2,10	4,96	0,67
$\mathbf{B}_{tot}$	µg/l		< 30	30	30	48	< 30	< 30	< 30	60	100	36
$\mathbf{Ba}_{tot}$	µg/l		41	81	122	89	55	12	51	62	110	13
$\mathbf{Cd}_{tot}$	µg/l		0,45	0,14	0,12	0,12	0,38	1,00	<0,10	<0,10	0,22	0,59
$\mathbf{Co}_{tot}$	µg/l		0,36	0,23	< 0,2	0,25	0,31	0,50	3,60	0,5	0,5	0,48
$\mathbf{Cr}_{tot}$	µg/l		1,2	< 1,0	< 1,0	1,5	1,5	1,5	1,0	1,0	1,0	1,0
$\mathbf{Cu}_{tot}$	µg/l		7,2	4,2	4,7	7,2	7,0	3,6	5,6	1,9	2,0	1,1
$\mathbf{Fe}_{tot}$	µg/l		603	451	611	474	429	352	800	118	310	170
$\mathbf{Hg}_{tot}$	µg/l		< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	0,25	0,03	0,03	0,05	0,05
$\mathbf{Mn}_{tot}$	µg/l		28	32	10	22	30	226	642	63	95	62
$\mathbf{Mo}_{tot}$	µg/l		< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	0,5	0,5	6,5	1,8	0,5
$\mathbf{Ni}_{tot}$	µg/l		4,0	2,0	2,3	2,8	2,9	5,2	11	2,0	2,3	1,2
$\mathbf{Pb}_{tot}$	µg/l		13,3	3,2	1,2	6,2	29,7	5,0	1,0	1,1	2,0	3,7
$\mathbf{Sb}_{tot}$	µg/l		4,5	1,6	2,5	2,9	6,8	6,2	0,8	2,1	1,0	0,4
$\mathbf{Se}_{tot}$	µg/l	3	< 0,80	< 0,80	< 0,80	0,98	0,98	< 0,80	< 0,80	2,90	< 0,80	1,00
$\mathbf{Si}_{tot}$	µg/l			4.436	4.407	4.903	5.218	n.a.	n.a.	n.a.	n.a.	n.a.
$\mathbf{Tl}_{tot}$	µg/l	0,2	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	0,10	0,10	0,10	0,10	< 0,05
$\mathbf{U}_{tot}$	µg/l		0,05	0,07	< 0,05	< 0,05	0,74	0,25	1,26	4,69	0,83	0,25
$\mathbf{V}_{tot}$	µg/l		< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	0,46	1,00	2,76	5,00	0,50
$\mathbf{Zn}_{tot}$	µg/l		53	15	20	29	37	36	18	53	18	33

For the dissolved phase two different kinds of EQS are defined: The AA-EQS (annual average), which is defined as the arithmetic mean of the concentrations measured on different times during the year and on the other hand the MAC-EQS, which is defined as the *m*aximal *a*llowable *c*oncentration. For the dissolved phase EQS are determined for cadmium, nickel, lead and mercury. However, the latter is of minor importance for the Harz region. For cadmium, in all catchment areas the calculated background concentrations exceeds the AA-EQS, in the Weser catchment area even the MAC-EQS. For nickel the background concentrations exceed the MAC-EQS in the Selke catchment area and for lead in the western catchment areas of the Oker, Oder and Sieber.

Table 3: *Selected geogenic background concentrations of the dissolved phase in the catchment areas of the Harz mountains, calculated as the arithmetic mean of the 90%-percentile of the single water bodies, and EQS-values* (*italics*: concentrations > AA; ***bold and italics***: concentrations > AA and MAC).

	Unit	EQS	Oker P90	Oder P90	Sieber P90	Söse P90	Innerste P90	Wipper P90	Selke P90	Helme P90	Bode P90	Weser P90
$\mathbf{Ag}_{dis}$	µg/l		0,24	0,08	0,10	0,12	0,13	< 0,02	0,07	0,05	0,05	0,06
$\mathbf{Al}_{dis}$	µg/l		358	354	308	86	108	31,4	23,8	< 10	110	546
$\mathbf{As}_{dis}$	µg/l		0,8	1,1	1,1	< 0,5	< 0,5	3,1	3,7	1,5	0,9	2,1
$\mathbf{B}_{dis}$	µg/l		15	29	21	44	15	15	20	83	148	30
$\mathbf{Ba}_{dis}$	µg/l		49	67	91	82	45	16	20	51	110	75

	Unit	EQS	Oker P90	Oder P90	Sieber P90	Söse P90	Innerste P90	Wipper P90	Selke P90	Helme P90	Bode P90	Weser P90
Cd_{dis}	µg/l	AA 0,08 MAC 0,45	*0,40*	*0,22*	*0,24*	*0,10*	*0,20*	*0,17*	*0,30*	*0,10*	*0,13*	***0,47***
Co_{dis}	µg/l		0,21	< 0,20	< 0,20	< 0,20	< 0,20	< 0,20	0,82	1,04	< 0,20	0,50
Cr_{dis}	µg/l		< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	2,0	1,6	1,8	1,0
Cu_{dis}	µg/l		2,4	2,0	2,4	3,2	3,5	1,2	2,7	1,3	3,1	6,5
Fe_{dis}	µg/l		323	346	701	88	90	30	504	51	200	210
Hg_{dis}	µg/l	AA 0,05 MAC 0,07	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01
Mn_{dis}	µg/l		76	35	59	9,0	19	112	346	59	42	37
Mo_{dis}	µg/l		< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	7,2	0,5	0,5
Ni_{dis}	µg/l	AA 20 MAC 20	3,1	1,2	1,4	2,1	1,9	3,1	***41***	15,4	2,2	3,3
Pb_{dis}	µg/l	AA 7,2 MAC 7,2	***7,9***	***8,1***	***12,11***	1,8	3,9	0,3	2,2	0,5	0,7	2,3
Sb_{dis}	µg/l		n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1,0	1,0
Se_{dis}	µg/l		< 0,8	< 0,8	< 0,8	< 0,8	< 0,8	< 0,8	< 0,8	< 0,8	< 0,8	< 0,8
Si_{dis}	µg/l		5.225	4.593	3.304	4.898	4.698	n.a.	n.a.	n.a.	n.a.	n.a.
Tl_{dis}	µg/l		0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
U_{dis}	µg/l		< 0,05	0,06	< 0,05	< 0,05	< 0,05	0,12	< 0,05	4,00	0,78	0,09
V_{dis}	µg/l		0,8	< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	0,3	0,5	0,5	0,5
Zn_{dis}.	µg/l		36	17	24	26	30	110	16	44	13	12

5. Discussion

The results show, that the rivers in the Harz Mountains are naturally characterized by relatively high metal concentrations. However, the spatial distribution of the metals for the water bodies can strongly differ for the total phase and the dissolved phase (see figures 3 and 4). The most important origin for the metal concentrations in the water bodies are the geogenic conditions in the Harz Mountains. The high concentrations of iron, zinc, copper reflect the mineral resources, which are mined in the Harz Mountains. The figures 3 and 4 show that the western Harz is a hotspot for high silver and lead concentrations; it is also an important region for the mining of both metals. Also metals, which are of lower importance for the mining in the Harz can be found in the surface waters, like, barium, originating from baryte mineralisation, antimony, manganese, often associated with iron, from oxidic manganese-ores or nickel and arsenic from arsenic nickel-cobalt ores or silver-rich ores. For elements like iron, aluminium or silicon, the weathering of rocks is an important source of their occurrence in the surface waters. For the other elements the origin of their occurrence in the rivers are metallogenic mineralizations.

In addition to the geogenic conditions in the Harz Mountains also the atmospheric deposition must be considered as source for the background concentrations in the surface waters. The input by atmospheric deposition is of importance for copper, cadmium and zinc. For lead the atmospheric deposition declined in the last decades strongly.

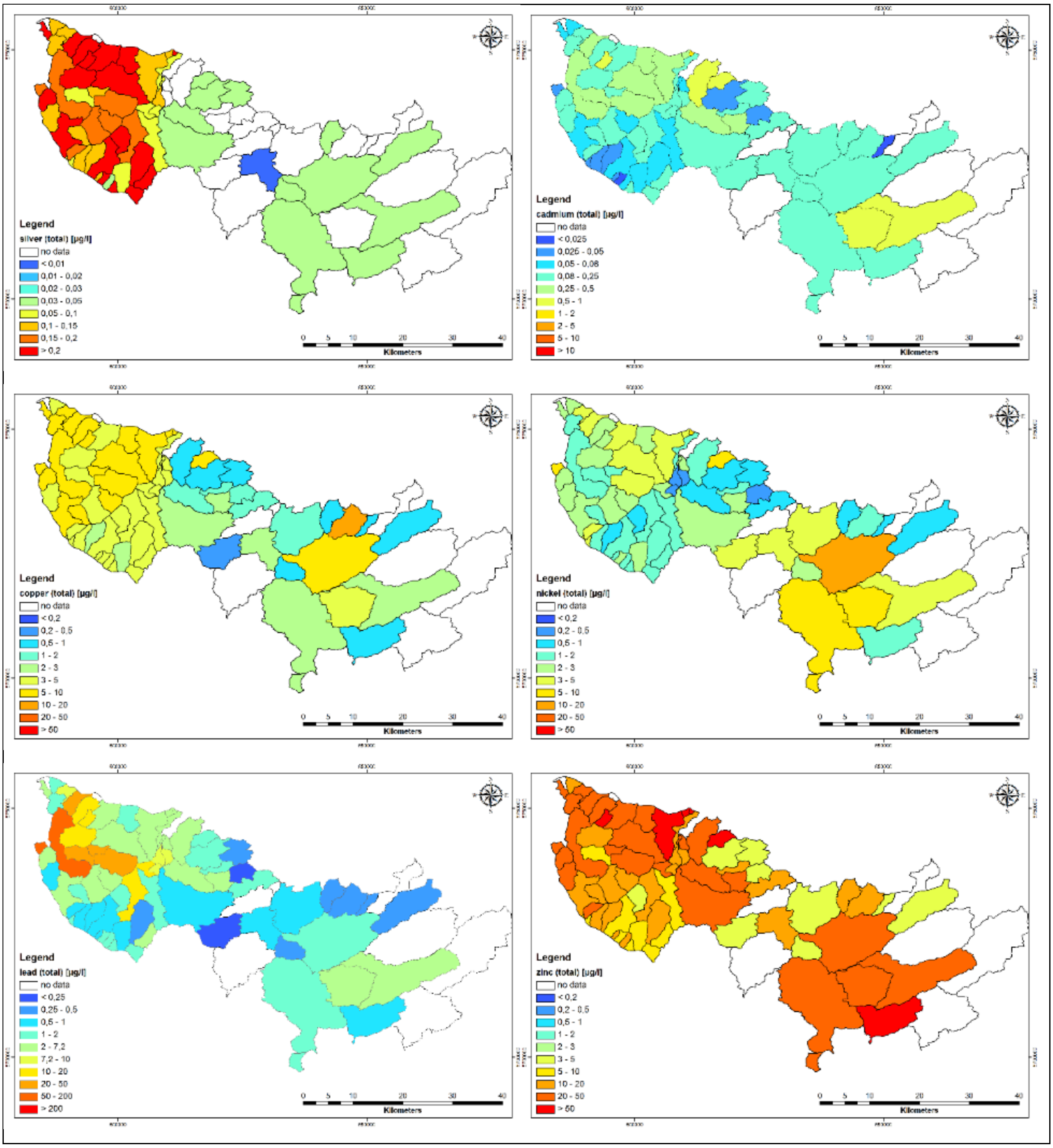

Figure 3: *Geogenic background concentrations of the total phase for cadmium, copper, nickel, lead and zinc in the catchment areas of the Harz Mountains.*

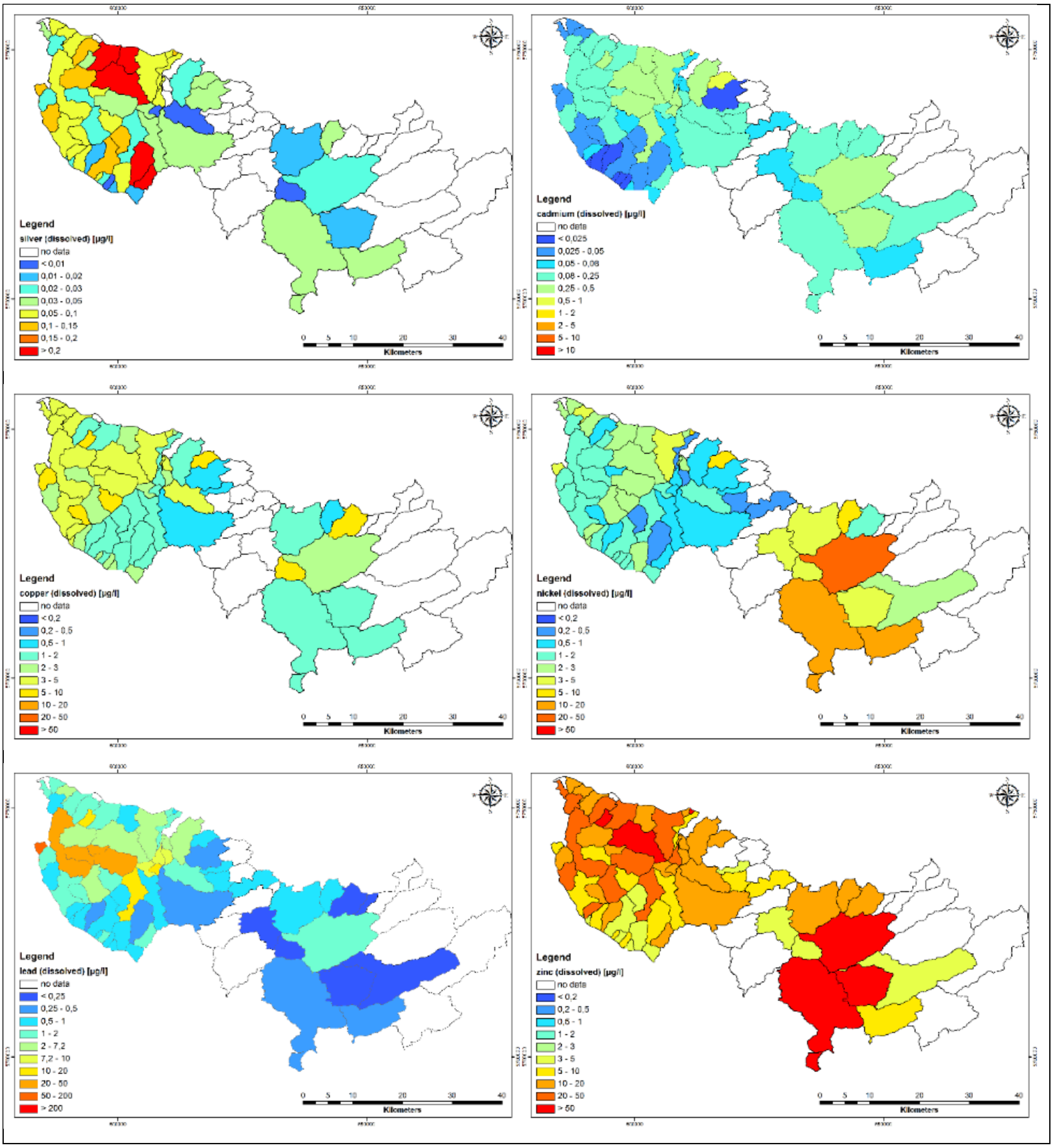

Figure 4: *Geogenic background concentrations of the dissolved phase for cadmium, copper, nickel, lead and zinc in the catchment areas of the Harz Mountains.*

6. Conclusions

The Harz Mountains can be described as a geogenic metallogenic region. Thus, it is expected that because of high geogenic background concentrations in the rivers less stringent objectives for the WFD could be determined. To proof the assumption of high geogenic background concentrations an assessment was made to determine the background concentrations for several metals in the total phase and the dissolved phase in several water bodies of the Harz Mountains. The results show, as for a metallogenic riverine landscapes expected, a high background concentration for several metals. In the total phase, the calculated background concentration of silver exceeds the EQS in all catchment areas of the western Harz. In the dissolved phase the calculated background concentration of cadmium exceeds the AA-EQS in all catchment areas and the MAC-EQS in the Weser catchment area. Moreover the MAC-EQS of the dissolved phase is also exceeded for nickel in the Selke catchment area and for lead in the catchment areas of Oker, Oder and Sieber. Thus the results of the assessment confirm the assumption of high geogenic background concentrations of metals in the water bodies of the Harz Mountains and can serve as a basis for the determination of exemptions for the implementation of the WFD.

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