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Determination of the Geogenic Metal Background in Surface Water: Benchmarking Methodology for the Rivers of Saxony-Anhalt, Germany

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Abstract: Geogenic concentrations are defined as those concentrations that represent the natural background without any anthropogenic influence. The paper describes a statistical method for determining geogenic metal concentrations in rivers based on the concept of "aggregated riverine landscapes" (ARLs), which applies to all rivers in the Federal State of Saxony-Anhalt (Germany). The methodology includes the pre-selection of existing data by eliminating all sampling locations from the database which have anthropogenic influence, the GIS-based allocation of the sampling locations with respect to the respective ARL being the evaluation units, and the assessment of the geogenic background by statistical calculation of the 90th percentile. After validation of the methodology, the existing database was complemented by additional measurements for regions with data gaps. About 85,000 records of water samples, 1400 records of sediment samples, and 920 records of suspended particulate samples were used for the determination of the geogenic metal concentrations in the rivers of Saxony-Anhalt. The investigation included the parameters Al, Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Ti, U, V, and Zn. The investigation results offer the determination of regions with increased background levels for certain metals or metalloids in Saxony-Anhalt.

Keywords: geogenic metal concentrations; WFD exemptions; assessment method development

1. Introduction

The European Water Framework Directive 2000/60/EC (WFD) [1] is the basis for the integrated water policy in Europe. The key objective is holistic water management at the level of river basins based on a high level of protection of the aquatic environment, reflected by a "good status" by 2015. The WFD provides a number of exemptions that allow for less stringent objectives, including the extension of the implementation deadline beyond 2015, to a maximum of 2027. One of the potential reasons for an exemption is the elevated natural background concentration of metals in comparison to the Environmental Quality Standards (EQS). Maximum permissible pollutant concentrations have been defined in Directive 2008/105/EC [2]. This Directive and the amending Directive 2013/39/EU [3] provide the EQS for non-synthetic pollutants, such as metals and metalloids. Article 4 (Environmental

Objectives) [4] of the WFD and the Water Resources Act of Germany (WHG, especially Article 29 (Deadlines for the Achievement of the Management Objectives) [5], Article 30 (Deviating Management Objectives) [6], and Article 31 (Exemptions to the Management Objectives) [7]) allow, under certain conditions, an extension to the deadline for achieving the good status, or even to work against less stringent environmental objectives. Any deviation from achieving the "good status" needs to be justified and substantiated based on appropriate, evident, and transparent criteria, as listed in Article 4 (4)—Extension of Deadlines [8] and Article 4 (5)—Less Stringent Environmental Objectives [9] of the WFD [1]: (i) technical impracticability of measures; (ii) natural conditions that do not allow timely achievement of the environmental objectives; and/or (iii) disproportional cost. The criterion "natural conditions" includes conditions determined by natural processes. Elevated geogenic metal concentrations may be particularly caused by specific local conditions, such as natural features.

A generally accepted and standardized methodology for the assessment of geogenic background values for metals does not exist, despite being required for the WFD implementation. Although the competent authorities usually do have at their disposal a large hydrochemical database resulting from the surface water monitoring, the availability of information on the natural background is limited. In practice, the scope of the competent authorities for the implementation of the WFD is to select, in a replicable way, those data from the existing database which represent the geogenic background. Moreover, in the common monitoring programs, the regions that are under physico-chemical stress are usually much better investigated in terms of sampling locations than the non-polluted regions. Methodological approaches to determine the background of metal concentrations have been described in the literature for groundwater and river sediments, usually dividing between upstream and downstream areas [10–12]. Actually, these approaches do not refer to the natural background, but a local background concentration, and they are not applicable on the regional scale. However, rivers are subject to additional factors: the natural hydrochemical background concentrations in waters are influenced by the geological setting, the geochemical composition, adsorption on sediments, land use of the catchment areas, as well as indirect atmospheric deposition [13,14]. In the frame of the WFD implementation the term geogenic background refers exclusively to the reference status reflecting natural processes uninfluenced by human activities [15,16], and with this boundary condition differs from other approaches, like the assessment of historical mining influences, or consideration of the influence of diffuse pollution. Other investigations concerned the natural background of groundwater [17–19], with a focus on tritium-free old water, which has intense and long-term contact with the rock matrix. Further methods, which focus on the calculation of the geogenic background, are described in Matschullat et al. [20] and Matschullat et al. [21]—referring to the separation of geogenic background values for soil under diffuse pollution, as well metal baseline values in mining areas, like in Mast et al. [22], Hall et al. [23], Nordstrom [24,25]. In such investigations the geogenic background was concluded from statistical assessment. A few investigations referred to the natural background of surface water, noteworthy Zuurdeeg et al. [26] who used the 90th percentile and Laane et al. [27]. Crommentuijn et al. [28] adopted the approach in [26], but used a mean value instead of a 90th percentile. Ander et al. [29] calculated the 10th and 90th percentile, while Peters et al. [30] and Osté et al. [31] even concluded only the 10th percentile as a feasible approach, in order to exclude salt-water intrusions.

In order to harmonize the approach for the determination of the geogenic background in the river systems and water bodies in Germany, the German National Environmental Agency defined the "riverine landscapes" (RLs) according to the results of an investigation by Briem [32] as evaluation units for Germany in 2001. An RL is understood to be a landscape area that is largely homogeneous with respect to the geological and geomorphological formations, but may contain several types of water, depending on the soils, the hydrology, or the position in the longitudinal course of a water body. A further subdivision of the water bodies is due to the altitude, particularly with respect to lowland and mountain water bodies. Within these two natural habitats, there is a large variety of regional rivers and river types, which differ in the valley forms, the course of the river, the type of bottom substratum, and the annual discharge distribution. An RL includes the ecosystems in and around the area of a river, and may also be defined as a network of rivers and surrounding land. The RLs according to Briem [32] are a very detailed set of water body types that in their original form were considered to be too detailed for the assessment of hydrochemical aspects due to their strong sub-differentiation. In order to overcome this constraint, aggregated riverine landscapes (ARLs) have been developed by Schneider et al. [33,34], which summarized RLs of similar geochemical characteristics in terms of certain levels of differentiation, including the sublevel of differentiated riverine landscapes (DRLs). The resulting RLs included the calcareous-dolomitic type, saliniferous, siliceous, and sandy-clayey type as well as bogs/bog riverside meadows. Even all RL types are generally characterized by a gross database characterized through a high degree of aggregation, one of the basic criteria was the availability of at least 10 samples in order to ensure statistical representativity. The definition of the RLs takes into account the requirements of the WFD with regard to ecological quality components, namely structural and hydromorphological requirements, and do have only a very general reference to the geological setting of the region. The German National Environmental Agency defined the RL as the compulsory evaluation unit for the assessment of geogenic background values for the purpose of the WFD implementation in Germany in order to ensure (a) a comparable approach in all Federal States; and (b) the reference to the ecological assessment of water bodies [33]. The administrative unit of a water body is a subunit of a catchment as the European evaluation unit of the WFD. Under consideration of the time schedule for the implementation of the WFD, which goes along with a limited budget of time and financial resources, the resulting practical requirement was to develop a methodology to conclude the geogenic background values from the existing monitoring databases of the competent authorities in order to determine the areas for the application of WFD exemptions. Saxony-Anhalt was one of the pilot regions for the development of such a methodology.

In the frame of a geochemical assessment in [34] the insufficient consideration of the geological setting was considered a deficiency of the original RL concept, taking into account that geogenic metal concentrations of surface water can be closely related to the geochemical and mineralogical composition of rocks and sediments in the catchment. The geogenic metal concentrations calculated by Schneider et al. in 2003 [33,34], using the very raw database for Germany that was available in 2001/2002, already led to the conclusion of the existence of regions with increased metal background concentrations in surface waters in Germany. The conclusion was the definition of a further RL type: the metallogenic riverine landscape [35], which complemented Briem's RLs [32]. Based on this additional RL, certain German regions with a geogenic metal influence have been identified. These include the Ore Mountains (Saxony), the Black Forest (Baden-Württemberg), the Harz Mountains (Lower Saxony and Saxony-Anhalt), and the Rhenish Slate Mountains (North Rhine-Westphalia, Rhineland-Palatinate, Hesse, and the Saarland).

In addition to the approach of Schneider et al. [33,34], further methodologies were pre-evaluated for the calculation of the geogenic metal background in Saxony-Anhalt. The considered methodologies were the runoff-concentration-analysis according to Hellmann [36], the component's separation according to Kunkel et al. [37], the procedure according to Schleyer and Kerndorff [17], the evaluation of sediment data through geoaccumulation-index assessment according to Müller [38], further developed in Greif et al. [39], as well as a hydrogeochemical modeling approach. In order to obtain reliable information about the geogenic metal contents in the rivers of Saxony-Anhalt, a GIS-based statistical method was developed based on the scale of the ARL. The information on the geogenic metal concentrations shall be used for the provision of 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. For the investigation existing data provided by the State Authority for Flood Protection and Water Management of Saxony-Anhalt (LHW) were used, complemented with additional lab measurements. The methodology was developed for LHW in the period 2009–2013. The developed method was validated to be applicable, representative and transferable. It has, meanwhile, also been applied in several regions of Germany, such as the West Harz in Lower Saxony [40], Thuringia, and North-Rhine-Westphalia.

2. Materials and Methods

The results of the pre-evaluation indicated that an assessment of each sampling location of the existing database will be necessary in terms of the land use and other potential anthropogenic influences. This was done using a GIS-based approach, followed by manual verification. Influenced sampling locations were eliminated from the database in the pre-selection step. Further, the approach should be sufficiently applicable to also consider the inhomogeneity of the database in terms of seasonal data variability and sampling frequency, which usually characterizes the monitoring data of the competent authority, particularly historical data. The majority of the samples was taken at least yearly in the official monitoring program, some samples even more often. In order to ensure the robustness of the methodology especially with respect to the inhomogeneity of the database, a statistical method was preferred to separate background and anthropogenic populations instead of other approaches, like cumulative probability plots. The basis for the applicability of such methods is usually not feasible for the database of the competent authorities, since (a) the database is usually very large, and (b) the values are not uniformly distributed. The applied pre-selection procedure comprises the following general steps:

- A double procedure for the elimination of all sampling locations from the database which have anthropogenic influence,
- GIS-based allocation of the sampling points with respect to the respective "aggregated riverine landscapes", being the evaluation units,
- Assessment of the geogenic background data by calculation of statistical parameters with data pre-selection in order to extract the anthropogenic uninfluenced rivers per AGL, and
- Validation of the background data using the Germany-wide background levels calculated by Birke et al. [41] as a benchmark.

The procedure for elimination of sampling locations concerns a double procedure, which, as the first step, was an automatic GIS-based assessment of sampling locations, where information was available in digital format (e.g., agricultural land use, pollution sources). This step was followed by a supplementary detailed manual elimination procedure, where information on mines, shafts, etc., was considered and led to the exclusion of sampling locations.

The "Geochemical Map of Germany" [41] was used for comparison of the calculated geogenic concentrations to the Germany-wide background levels (validation). In parallel, a search for further historical data sources of the Saxony-Anhalt region was prepared. Most of the searched databases proved to be inapplicable for the purpose of geogenic metal concentrations in the rivers of Saxony-Anhalt due to several reasons: the data have been obtained for soils [20,21] or sediments [42], they have been obtained for neighboring geographic regions, especially Lower-Saxony, showing an anthropogenic influence by acid rain [20], or historical data which have been secret due to former Soviet-union exploration activities in certain regions, like the Harz Mountains [42]. This situation led to a remaining database for the validation of the investigation results, the "Geochemical Map of the Metal Concentrations in the Rivers of Germany" according to Birke et al. [41] applicable for the benchmarking process, which is based on the 50th and 90th percentiles. The validation procedure using the natural background data in Birke et al. [41] as a benchmark indicated that the P(90) values represented a realistic and plausible concentration level, even the data aggregation level of the data of Birke et al. [41] is very raw. The data pre-selection of the P(90) approach led to the identification and exclusion of samples that are subject to anthropogenic influences from the total database. Table 1 summarizes the different characteristics of the procedures with and without pre-selection of the sampling locations that were applied simultaneously.

Table 1. Specific criteria for the geogenic background.

Criterion	Statistical Approach with Pre-Selection	Procedure without Pre-Selection
Genetic classification of data	aggregated riverine landscapes by Schneider et al. [33,34]	none
Preselection of database	yes	no
Statistical parameter for derivation of geogenic background	50th percentile (median) 90th percentile	50th percentile (median) 84.1st percentile (according to [17]) 90th percentile
Advantage	Genetic classification of data (here ARLs) allows for the allocation of areas with increased concentrations to the geological setting Data for large data sets (>80,000) can be processed (meta catchment scale, here about 300 water bodies with several sampling locations) through the use of GIS Existing data from county monitoring activities can be included after verification and selection Sensitive also to very low detection limits as usually the geogenic concentrations are low	Served for the separation of the anthropogenic proportion of the concentration of an element in a groundwater from the geogenic proportion, regardless of the geological setting [17]
Disadvantage	Database for suspended matter needs to be improved	Methodology derived from about 2800 datasets from groundwater extraction wells for groundwater [17], not applicable for surface water No pre-selection causes that there is no consideration of external effects which can affect the geogenic concentration Genetic classification of data is not foreseen

For the pre-selection procedure it was assumed that natural water quality occurs when the headwaters are originating in forests (≥95% forest) without anthropogenic influence, considering the site-specific lithology as discussed in Norra et al. [43]. Furthermore, the atmospheric deposition, as well as the soil erosion induced by acids (e.g., nitrate, cadmium and zinc), should be considered [43]. For the pre-selection of the database the following selection criteria were used:

- headwaters are originating in woodlands (≥95% forest),
- exclusion of sampling locations affected by point sources, and dischargers, as well as diffuse sources (agricultural land use, transport); point sources were considered sampling locations, in whose catchment areas mining activities, like mines, mining piles, and smelters are identified, as well as contaminated sites, settlements, and industry, and
- increased concentrations of nitrate (>5 mg/L), ammonium (>0.5 mg/L) and phosphate (>10 µg/L) as indicators for the identification of anthropogenic influence, including analysis of selected sampling locations in terms of the concentrations of NO_3-N, NH_4-N, and PO_4-P as indicator parameters for agricultural land use.

Land use, location, and size of the catchment area, as well as the location of direct dischargers were analyzed by the use of Geographic Information Systems GIS [44]. Further, GIS was used for the spatial visualization of the results on the level of water bodies (WB), as required by the WFD, through assignment of the results for geogenic background concentrations of total metals and metalloids to WBs in a catchment area, under consideration of the proportion of the RLs. The resulting value for a catchment area was the value that was used for the benchmarking process with the data according to Birke et al. [41]. A sample for the assignment of the determined geogenic background concentrations of total metals and metalloids (P90) to the catchment areas of the WFD is given in Figure 3 (Section 3.4).

Using the described approach, the available data pool for river sampling locations in Saxony-Anhalt covering the sampling period 1993–2012 was reduced from a total of 2033 to 299 locations. Furthermore, the database was completed with external data from various state and federal government institutions (Regional Authority for Waste Site Assessment, Elbe Catchment Working Group, Federal Institute of Water Technology, and the National Environmental Agency). After the data screening and plausibility verification, approximately 85,000 records of water samples, 1400 records of sediment samples and 920 records of suspended particulate samples were left. While results for the water phase are rather abundant, samples of suspended particulate matter are much scarcer: no data could be analyzed for calcareous-dolomitic, metallogenic, and saliniferous types of the riverine landscapes. Even for the remaining aggregated riverine landscapes, only an insufficient amount of data of suspended particulate matter was available for the statistical assessment.

After the validation of the methodology and the regional gap analysis, the database was complemented by 186 additional measurements carried out at certain sampling locations for regions or riverine landscapes with data gaps. The sampling was done according to DIN 38402-15 (DEV A15). Data gaps were considered in regions where the existing database did not reach the necessary density for a representative statistical analysis, which was especially valid for areas in the upstream part of the water bodies. The samples for the investigation of the filtered water phase were processed with a 0.45 µm membrane filter for separation of the particulate matter. The samples were stored in HDPE bottles, except for the Hg analysis, which used brown glass bottles. The conservation of the samples was done with HNO_3, except for Hg for which $K_2Cr_2O_7/HNO_3$ was used, and Fe, for which H_2SO_4 was used for conservation.

The analytics were carried out using the following methods: ICP-OES: inductively coupled plasma with optical emission spectroscopy $^{(1)}$, ICP-MS: mass spectrometry with inductively-coupled plasma $^{(2)}$, and AAS: atomic absorption spectrometry $^{(3)}$. The following metals were considered (the superscripts indicate analysis method as per the list above, as well as the lowest detection limit (DL) for the respective parameter): aluminum^1 (10 µg/L), antimony^2 (1 µg/L), arsenic^2 (0.5 µg/L), barium^1 (10 µg/L, beryllium^2 (0.05 µg/L), lead^2 (0.5 µg/L), cadmium^2 (0.02 µg/L), chromium^1 (1 µg/L), iron^1 (50 µg/L), cobalt^1 (0.2 µg/L), copper^1 (0.2 µg/L), manganese^1 (10 µg/L), molybdenum^2 (0.5 µg/L), nickel^1 (1 µg/L), mercury^3 (0.01 µg/L), selenium^2 (0.8 µg/L) silver^2 (0.02 µg/L), thallium^2 (0.05 µg/L), titanium^1 (5 µg/L), uranium^2 (0.05 µg/L), vanadium^1 (0.3 µg/L), zinc^1 (10 µg/L), and tin^2 (1 µg/L).

Due to different data sources needed (a) to deal with different DLs and (b) to convert non-detects to 1/2 DL for data assessment, with respect to the DLs, it must be noted that partial historical data could nearly not be used for the assessment of the geogenic background values since the DL was much higher than the recent EQS requirements of the Surface Waters Ordinance of Germany [45]. This led to the situation that the majority of historical measurements for geogenic metals in surface water could not be directly compared with the recent results. The problem with DLs above the EQS applied especially for the parameters cadmium, mercury, nickel, and lead. After the data search and the sampling campaign, the following numbers of samples (indicated in brackets) over all RLs for the filtered water samples were available: aluminum (45–106), antimony (44–106), arsenic (44–101), barium (18–42), beryllium (32–87), lead (46–225), cadmium (46–246), chromium (44–90), iron (44–96), cobalt (44–96), copper (44–90), manganese (44–90), molybdenum (44–90), nickel (56–301), mercury (41–231), selenium (44–90), silver (44–106), thallium (42–90), titanium (34–90), uranium (44–95), vanadium (44–90), zinc (30–77), and tin (10–58).

Since a spatial data assessment is always associated with a reduced data volume resulting from aggregation, the determination of geogenic background concentrations was carried out using the AGLs. Although this classification scheme results obviously in a unification of divergent geochemical areas, it ensures a statistically robust and comprehensive derivation of background concentrations. The aggregated riverine landscapes in Saxony-Anhalt according to Briem [41], and the geological setting are shown in Figure 1.

Almost all of Saxony-Anhalt lies within the North European Plain, and its geological setting is dominated by results of eras of glaciation, leaving behind sediments of Holocene and Pleistocene age [46]. The Elbe River flows in the central part of Saxony-Anhalt, while the south is drained by two of the Elbe's tributaries, the Saale and Mulde Rivers. Holocene alluvial sediments in the floodplains and sedimentary rocks comprised of sandstone at the valley slopes dominate the geological setting in the north and northwestern part. The southwest portion of Saxony-Anhalt includes parts of the Harz Mountains, adjacent foothills, and the fertile Harz Foreland, including copper shale-rich locations.

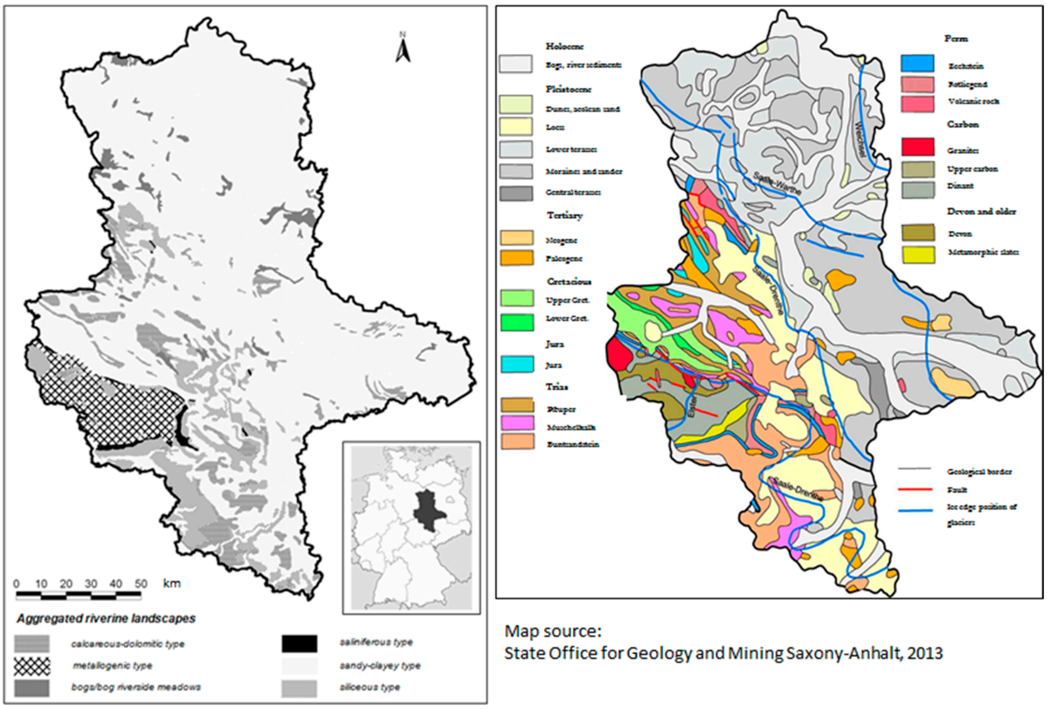

Figure 1. Aggregated riverine landscapes in Saxony-Anhalt, and the geological setting.

The Harz Mountains form the highest elevation in Saxony-Anhalt, and have been formed during the Variscan orogeny 300 million years ago by folding, uplifting, and erosion [47]. 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. Geologically and morphologically, the Harz Mountains can be separated into three areas: Upper Harz, which is located in the neighboring Lower Saxony; Central Harz, which proportionately belongs to Lower Saxony and Saxony-Anhalt, and Lower Harz, which is located in Saxony-Anhalt, differ in their geological settings and the magmatic, tectonic, sedimentary, and erosional genesis. All three geological units of the Harz Mountains show the occurrence of vein deposits with different mineralogical characteristics, which have been formed during the younger tectonic expansion. This characteristic lead to the classification of metallogenic RLs, indicated in Figure 1 with cross-hatching. In the Central Harz, silver-antimony-sulphosalts are of importance. In the south and southwest there are quartz-magnetite-chalcopyrite veins, quartz-hematite veins, barite-hematite veins, and barite veins. In the Lower Harz are important deposits of pyrite, siderite, and fluorite [48]. Lead-zinc ores are not as significant as in the Upper Harz. In the Middle Ages, the mining in the Harz Mountains reached a prosperous period. The main products of the mining activities were silver, copper, lead, and iron and, since the 19th century, also zinc [49].

3. Results

3.1. Comparison of Results without the Pre-Selection of Data

The results of the values obtained without pre-selection resulted in increased values for the natural background, which, after the spatial application to WBs, have not been comparable to the level of the validation data by Birke et al. [41]. Consequently, anthropogenic influences are not separated from the geogenic concentrations and led to exceedance of the EQS. In particular, for the calculated concentrations of cadmium, lead, and zinc in the water phase, the resulting values are still characterized by anthropogenic influences.

The assessment of the methodology has led to the conclusion that, for the assessment of the background values, the natural concentrations, represented by sampling locations with geogenic origin, must play a central role and a pre-selection of the data is necessary. Further, it was concluded from the pre-evaluation that the database must be complemented with supplementary analytical data, which led to the investigation program described above, in order to also improve the statistical liability. Anyhow, a poor database exists for the suspended phase, which plays a larger role in the recent European water legislation than in the past. The validation with total phase benchmark data for Germany obtained from Birke et al. [41], expressed as geochemical background of Germany showing significant differences for Cd (0.08 μg/L—up to 10 times higher), Cr (0.19 μg/L—up to 10 times higher), Cu (0.68 μg/L—up to five times higher), Ni (2.13 μg/L—up to three times higher), and Zn (0.47 μg/L—partially more than 100 times higher).

3.2. Results of the Statistical Analysis with Pre-Selection of the Data

The modified statistical procedure with pre-selection of the data is based on the assessment of geogenic background concentrations of the 50th and 90th percentiles. The sampling locations with anthropogenic influences were identified and excluded by means of pre-defined selection criteria before the qualified database was subjected to further statistical analysis: in this way 249 potentially geogenic measuring points were selected. The applicability of the method was again tested through validation. While the P(50) percentile results in concentration levels that are too low, validation using the general data Birke et al. [41] as a benchmark showed that the P(90) values represent the geogenic background properly. The calculation results are shown in Tables 2–4.

Table 2. Geogenic background concentrations of total metals and metalloids in the rivers of Saxony-Anhalt classified by the aggregated riverine landscapes (pre-selection of data, 50th and 90th percentiles, for all elements the database is $n > 20$; *italics* represent data below the detection limit).

Total Phase [μg/L]	Calcareous-Dolomitic		Siliceous		Metallogenic		Bogs/Bog Riverside Meadows		Saliniferous		Sandy-Clayey	
Parameter	**P(50)**	**P(90)**	**P(50)**	**P(90)**	**P(50)**	**P(90)**	**P(50)**	**P(90)**	**P(50)**	**P(90)**	**P(50)**	**P(90)**
Al	215	1110	25	157	120	278	25	68	25	84	25	346
Sb	0.5	1.0	0.5	1.0	0.25	1.0	0.55	1.0	*0.25*	1.0	1.0	1.0
As	0.25	1.08	0.5	2.64	0.25	2.5	0.57	1.6	0.8	*7.7*	0.5	1.61
Ba	70	100	66	240	14.5	56.5	60	146	13	110	57	87.6
Be	0.025	0.166	0.125	0.39	0.064	0.22	0.025	0.46	0.025	0.071	0.025	0.09
Pb	0.5	0.9	0.5	0.7	0.5	3.4	0.5	0.7	0.5	1.0	0.5	1.0
B	25	51	25	108	25.0	26.4	56	138	80	320	25	100
Cd	0.025	0.122	0.08	0.24	0.08	0.30	0.025	0.05	0.1	0.22	0.025	0.06
Cr	*1.0*	*1.0*	*1.0*	*1.0*	*1.0*	*1.0*	*0.1*	1.0	*1.0*	*1.0*	*1.0*	*1.0*
Fe	285	2337	25	787	160	664	800	1650	25	35	1000	3315
Co	0.2	1.76	0.3	1.0	0.5	6.5	0.1	1.0	0.1	0.5	0.23	1.2
Cu	1.0	1.0	1.0	18.0	1.0	3.5	1.0	2.9	1.0	1.0	1.0	1.4
Mn	88	235	5.0	180	41	290	160	380	5.0	20	229	758
Mo	*0.5*	*0.5*	1.0	5.9	*0.5*	*0.5*	0.5	1.2	0.5	*7.7*	*0.5*	*0.5*
Ni	2.0	6.85	1.0	31.0	1.0	5.5	1.0	2.1	1.0	2.5	1.0	3,4
Hg	0.025	0.025	0.025	0.025	0.015	0.05	0.01	0.04	0.01	0.025	0.01	0.025
Se	0.5	0.8	0.5	1.5	0.4	0.6	0.5	1.2	1.3	2.4	0.5	0.5
Ag	*0.05*	*0.05*	*0.05*	0.80	*0.05*	*0.05*	*0.05*	0.08	*0.05*	0.09	*0.05*	*0.05*
Ti	2.5	*2.5*	2.5	8.9	2.5	2.5	2.5	11.3	2.5	2.5	2.5	2.5
Tl	0.025	*0.01*	0.1	0.1	0.1	0.1	0.025	0.025	0.025	1.0	0.025	0.025
U	3.8	6.92	1.2	4.2	0.25	0.95	0.257	2.25	0,93	4.10	0.25	5.55
V	0.5	5.0	0.5	5.9	0.5	5.0	0.5	0.5	0.5	0.5	0.5	0.5
Zn	5.0	32.4	5.0	24.4	5.0	25.0	5.0	14.0	10.0	19.8	5.0	21.0
Sn	0.25	0.5	0.25	0.5	0.25	0.5	0.5	0.5	0.25	0.5	0.5	0.5

Table 3. Geogenic background concentrations for metals and metalloids in the filtered phase in the rivers of Saxony-Anhalt classified by the aggregated riverine landscapes (preselection of data, 50th and 90th percentiles, for all elements the database is $n > 20$; *italics* represent data below the detection limit).

Total Phase [µg/L]	Calcareous-Dolomitic		Siliceous		Metallogenic		Bogs/Bog Riverside Meadows		Saliniferous		Sandy-Clayey	
Parameter	**P(50)**	**P(90)**	**P(50)**	**P(90)**	**P(50)**	**P(90)**	**P(50)**	**P(90)**	**P(50)**	**P(90)**	**P(50)**	**P(90)**
Al	5.0	150	5.0	25	7.5	71	5.0	25	5.0	25	25	189
Sb	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
As	0.25	1.0	0.25	1.30	0.8	5.3	0.25	0.9	1.2	13.0	0.25	0.8
Ba	68	165	70	109	31.5	104	70	159	40	101	85	146
Be	0.025	0.06	0.025	0.325	0.015	0.203	0.02	0.025	0.015	0.062	0.025	0.025
Pb	0.5	0.5	0.5	2.9	0.5	2.8	0.5	0.5	0.5	1.3	0.5	0.5
B	54	277	29	110	20.5	38.0	60	154	94	385	73	108
Cd	0.025	0.376	0.05	0.28	0.13	0.45	0.025	0.025	0.052	0.28	0.025	0.05
Cr	1.0	4.0	*1.0*	2.2	0.5	2.0	0.75	1.8	1.0	4.0	1.0	1.4
Fe	*42.5*	*729*	40	252	*146*	*1039*	195	947	36	317	155	821
Fe(II)	15	306	15	253	140	477	364	1343	15	53	86	598
Co	0.1	2.2	1.0	0.8	0.1	8.1	0.1	0.8	0.1	1.8	0.1	1.2
Cu	1.0	4.0	1.0	23	1.0	4.4	1.0	4.0	1.0	7.1	1.0	2.9
Mn	5.0	156	5.0	81	100	1969	152	357	5.0	55	144	570
Mo	0.15	0.5	0.15	2.1	0.15	0.5	0.25	1.0	0.5	7.6	0.5	0.5
Ni	3.9	10.8	2.05	34.0	1.2	26.4	1.0	3.9	5.0	24.0	1.3	5.5
Hg	*0.005*	0.01	0.005	0.01	0.005	0.01	0.01	0.01	0.005	0.01	0.01	0.01
Se	0.5	2.5	0.5	1.4	0.4	0.5	0.4	0.5	1.9	11.2	0.5	1.5
Ag	0.05	*0.06*	*0.05*	0.14	0.01	0.05	0.01	0.05	0.05	0.18	0.05	0.05
Ti	2.5	6.0	2.5	6.1	*2.5*	*2.5*	2.5	2.5	2.5	14	2.5	4.1
Tl	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025
U	2.4	7.0	0.6	3.95	0.025	0.55	0.254	1.17	1.0	4.0	0.25	5.16
V	0.15	0.5	0.15	2.8	0.15	0.5	0.15	0.5	0.15	0.5	0.5	0.5
Zn	5.0	34.0	13.5	32.0	5.0	172	5.0	12.2	11.5	32.0	2.0	16.1
Sn	*0.5*	*0.5*	*0.5*	*0.5*	*0.5*	*0.5*	*0.5*	*0.5*	*0.5*	*0.5*	*0.5*	*0.5*

Table 4. Geogenic background concentrations of suspended particulate matter in the rivers of Saxony-Anhalt classified by the aggregated riverine landscapes (preselection of data, 50th and 90th percentiles, *italics* represent data below the detection limit).

Total Phase [mg/kg]	Siliceous		Bogs/Bog Riverside Meadows		Sandy-Clayey	
Parameter	**P(50)**	**P(90)**	**P(50)**	**P(90)**	**P(50)**	**P(90)**
Sb	-	-	-	-	*10*	*10*
As	*13*	*14.6*	38.1	45	*24*	*34.5*
Ba	-	-	-	-	*516*	*558.*
Be	-	-	-	-	*1.5*	*2.6*
Pb	*47*	*52.4*	55.1	77.66	45	109
B	-	-	-	-	*13.5*	*33.3*
Cd	*0.6*	*0.68*	4.4	5.58	0.9	1.31
Cr	*50*	*52.4*	126	210.8	65.5	109.1
Fe	*34,700*	*35,900*	205,000	233,200	126,500	228,900
Co	-	-	-	-	*16*	*21.4*
Cu	*89*	*96.2*	49	65.7	58	96.2
Mn	*2000*	*15,040*	16,800	35,200	4875	14,710
Mo	-	-	-	-	*1*	*2.5*
Ni	*28*	*28*	104	151.6	35.5	51.2
Hg	*0.4*	*0.4*	0.9	1.64	0.2	0.3
Se	-	-	-	-	*1*	*1*
Ag	-	-	-	-	*0.5*	*1*
Ti	-	-	-	-	*552*	*890.4*
Tl	-	-	-	-	*0.5*	*0.5*
U	-	-	-	-	*1.2*	*2.27*
V	-	-	-	-	*56*	*69.9*
Zn	*260*	*276*	850	1068	317	439,1
Sn	-	-	-	-	*5*	*5*

Comparing the calculated background concentrations for the filtered and total values in water shows some parameter differences, as expected. This is due to the different sizes of the database for filtered and total concentrations. The situation concerns especially Sb, Ba, Cd, Co, Ni, and Zn. For these parameters the number of samples for the total phase is, for the most riverine landscapes, four times larger than for the filtered phase. Further, a high scattering of the statistical data was observed for Ni and Zn in the total water phase of the calcareous-dolomitic, siliceous, and sandy-clayey riverine landscapes, while a low scattering was observed for Ni in bogs and riverside meadows, as well as for Zn in the saliniferous riverine landscape type. The results of the assessment with pre-selected data demonstrate an increased level of background concentrations for some elements in certain types of riverine landscapes. The Harz Mountains are certainly an important geochemical region, which was appreciated by a separate investigation of the geogenic background also taking into account the part of the Harz Mountains located in Lower Saxony as well [40,50].

3.3. Validation of the Results

The "Geochemical Map of the Metal Concentrations in the Rivers of Germany" according to Birke et al. [41] was used for the validation process of the calculated geogenic background for Saxony-Anhalt, containing as benchmark data minimum, maximum, and 50th and 90th percentiles values for metals and metalloids. The database was generated in the frame of the preparation of the "Geochemical Atlas of Europe" by Salminen et al. [51]. The German data are based on a low-density geochemical survey, covering one sample per 380 km^2. Each sample was analyzed for 53 inorganic and 8 organic parameters in stream sediments and for 75 parameters in surface water Birke et al. [41]. The results are visualized as GIS maps.

Table 5 shows the results of the comparison of the geogenic background concentrations of metals and metalloids in Saxony-Anhalt in comparison with the data of Birke et al. [41]. The span was defined from the lowest P(50) value of an ARL in Saxony-Anhalt as minimum to the highest P(50) value over all ARLs in Saxony-Anhalt, as documented in Table 2. The data of Birke et al. [41] do not consider a special type of evaluation unit (e.g., geology or morphology). The span was taken from the maximum and minimum P(50) values over the whole of Saxony-Anhalt. The relevant benchmark data of [41] for the comparison are the minimum values in order to exclude zones with anthropogenic influences.

Table 5. Span of the geogenic background concentrations P(50) of total metals and metalloids in the rivers of Saxony-Anhalt classified by the aggregated riverine landscapes in comparison with the data of Birke et al. [41] (for ARL with pre-selection of data, 50th and 90th percentiles, for all elements the database is $n > 20$), *italics* represent data below the detection limit.

Total Phase [μg/L]	Span over all Types of ARL in Saxony-Anhalt—with Pre-Selection		Span of the Data of the Geochemical Map for Saxony-Anhalt—without Pre-Selection		
Parameter	**Min P(50)**	**Max P(50)**	**Min P(50)**	**Mean P(50)**	**Max P(50)**
Al	25	215	1	10	250
As	0.25	0.8	0.19	1.5	4.5
Ba	13	70	9	30	80
Pb	0.5	0.5	0.02	0.2	1.1
B	25	80	20	60	350
Cd	0.025	0.1	0.005	0.05	0.3
Cr	*1.0*	*1.0*	0.03	0.2	1.3
Fe	25	1000	10	90	1800
Cu	1.0	1.0	0.4	1.1	6.0
Se	0.4	1.3	0.08	1.07	3.58
Ag	*0.05*	*0.05*	0.002	0.004	0.006
Tl	0.025	0.1	*0.002*	0.013	0.17
U	0.25	3.8	0.07	0.7	7
Zn	5.0	10.0	0.5	2.7	14

3.4. Spatial Visualization of the Results

First step of the spatial GIS visualization was the allocation of the ARLs to the water bodies and the topographic units (see Figure 2 for an example). It shows the eastern part of the Harz mountains which is located in Saxony-Anhalt with the allocation of the metallogenic ARL as well as the Mansfeld copper shale region on the foot of the Harz mountains where took place copper shale mining in the past. The Mansfeld area is characterized through a mixed ARL system, which consists of saliniferous and siliceous RLs.

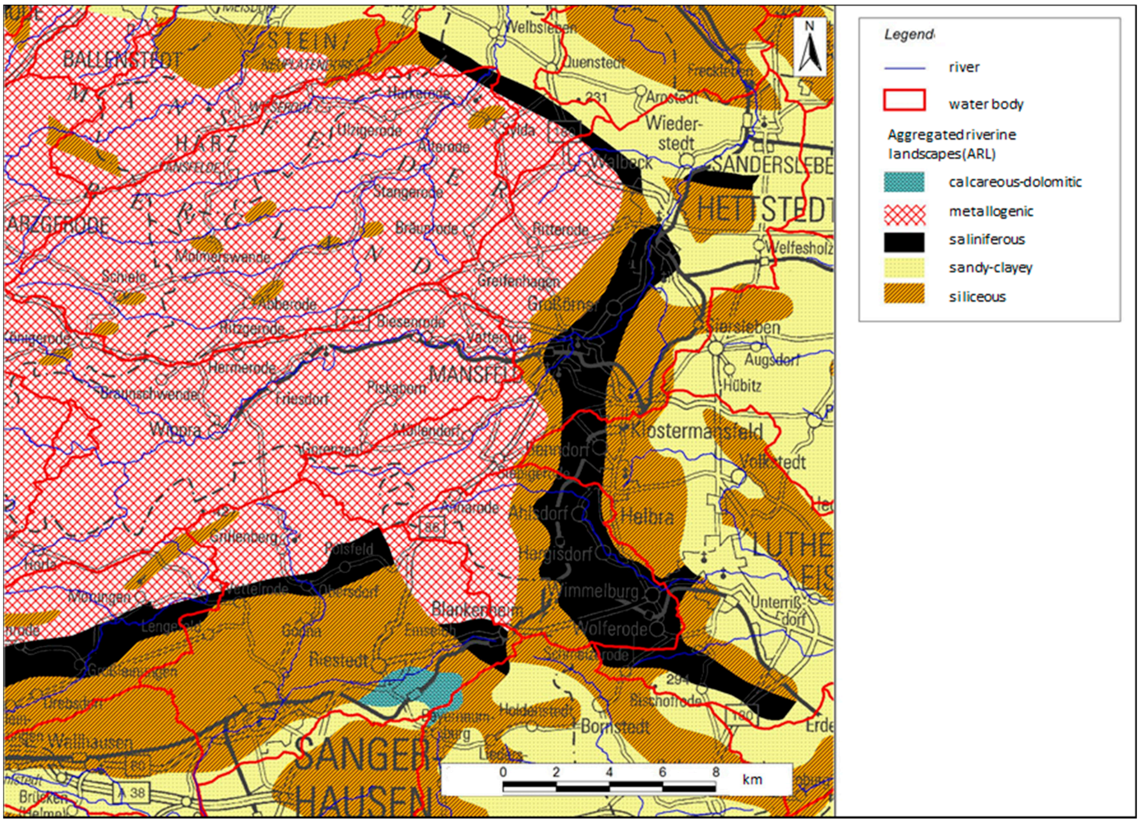

Figure 2. Aggregated riverine landscapes of the East Harz Mountains (metallogenic), and the Mansfeld copper shale area (saliniferous, siliceous).

Since the implementation of the WFD requires the assessment on the level of water bodies (WB), the determined background values must be assigned to WBs under consideration of the proportion of the ARLs in the WBs of a catchment area. Thus, the second step for the determination of the geogenic background values for water bodies was the allocation and assignment of the ARLs according to the respective percentage of their occurrences in the water body, which is the basis for the calculation of the geogenic background value for a WB under consideration of the lithology. The geogenic background value for a metal or a metalloid in a WB was allocated as the P(90) value of the respective dominant RL (see Figure 3). The dominant ARL is that ARL which dominates a WB in terms of the occupied area. In the case of more than one ARL within a WB, a grading from the dominant to the less important RL was considered in the GIS maps, expressed in the order of the listed ARLs, often resulting in a background value range for the respective WB. This approach is consistent with the proposal in [15] that "it is more realistic to view background as a range rather than an absolute value".

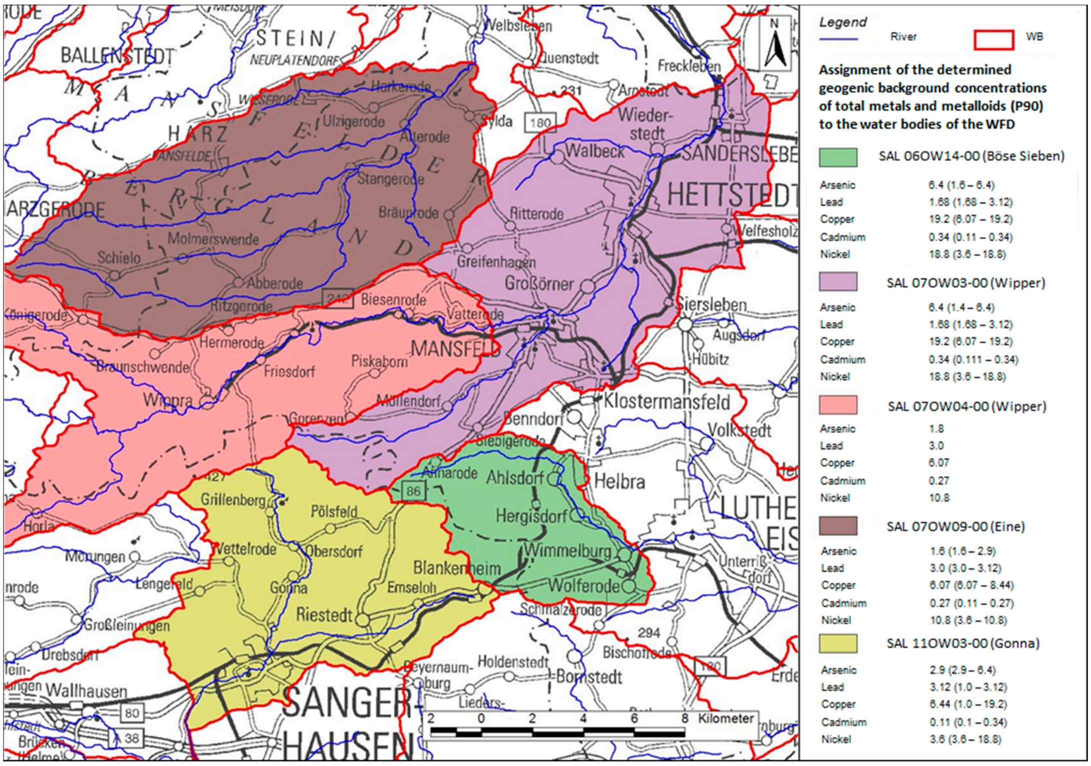

Figure 3. Sample for the determination of the geogenic background concentrations of total metals and metalloids (P90) of ARLs to water bodies.

4. Discussion

The comparison of the statistical analysis with and without pre-selection of the data examined in this paper has led to a preference of the statistical approach with the pre-selection of data. The optimal assessment criterion, validated through the data of Birke et al. [41] is P(90), while P(50) describes the average magnitude of the pre-selected data series. The P(90) approach takes sufficiently into account the geogenic fluctuation range of the geogenic background values of metals and metalloids in the ARLs. However, the median (P50) could also be used for deriving geogenic background concentrations, especially in the case of catchment areas with a homogeneous lithology. The comparison with the filtered phase benchmark data for Germany obtained from Birke et al. [41], expressed as the geochemical background of Germany as a validation data source showed, for some parameters, comparable results; for instance, Cd and Ni, and for some parameter values slightly above the average. Nevertheless, due to its size and location, Saxony-Anhalt is characterized by a high geological and geochemical variance. This leads to a major variability of element concentrations. This is generally also true for the results of the total metals and metalloids, and for some metals the DL in [41] was more sensitive than in the recent investigation. Anyhow, one shall consider that the Geochemical Map of Germany has a coverage of only one sample per 380 km^2.

The results underline that it is essential for surface water to consider only sampling locations that are clearly unaffected by human activity. The qualified assessment using the pre-selection of data through the assessment criteria of the 50th and 90th percentiles lead to methodologically plausible results. Sampling locations that are subject to anthropogenic influence were excluded. This way the assessment of the geogenic background concentrations was carried out on the basis of a quality-assured reduced data volume. Consequently, the results represent predominantly lower geogenic ranges. Comparison with the EQS showed only a few exceedances. The currently still small database will be gradually increased in the future through permanent monitoring of the selected sampling locations by the competent authority of Saxony-Anhalt.

The areas of Saxony-Anhalt, which are characterized by an increased natural background, are the Harz Mountains and peripheral areas in the south, as well as southeast. These areas have been subject to historical mining because (a) of the Lopinginan Zechstein group, which contains ore-metalliferous copper shale; and (b) the ores in the Paleozoic rocks of the Harz Mountains (even the main mining activities have been performed in the West Harz Mountains in Lower Saxony [50]). However, the bogs—which are found in the mountains—are also partly characterized by increased natural element concentrations, as they are geochemical sinks. The geogenic metal contents of the saliniferous type, as well as of the bogs, frequently exceed the background values of the metallogenic riverine landscapes. However, this contradicts the characteristics of the metallogenic type that is associated with a separate ARL type due to its metal related and crystalline characteristics [35]. The reasons for these results are to be found in the geochemical genetic characteristics of the different riverine landscape types. Both types of riverine landscapes (saliniferous and bogs) are subject to reducing (oxygen-deficient) redox conditions in their formation. Climatic influences are of minor importance as the Harz Mountains are a geological fault block, which leads to the situation that most of the precipitation falls in the West Harz Mountains in Lower Saxony. Overall, Saxony-Anhalt is a federal state with a low rainfall. The boundary condition that dominates the geogenic background concentrations in Saxony-Anhalt is the geochemistry of the geological setting. Mining for ore does not occur anymore since the re-unification of Germany.

Table 6 provides an overview of the riverine landscapes where geogenic background values were determined, which partially exceed the EQS of the Surface Waters Ordinance of Germany (OGewV) [45].

Table 6. Comparison of the P(90) values of the aggregated riverine landscapes with the EQS of the Surface Waters Ordinance of Germany (OGewV); results of the filtered water phase.

Para-Meter [μg/L]	EQS 2011/ Since 2015	Calcareous-Dolomitic	Metallogenic	Bogs/Riverside Meadows	Saliniferous	Sandy-Clayey	Siliceous
As	–/1.0	1.0	5.3	0.9	13.0	0.8	1.3
Ag	0.02/0.02	0.06	*0.05*	*0.05*	0.18	*0.05*	0.14
Cd	0.08–0.25 */0.15	0.376	0.450	*0.025*	0.280	0.050	0.280
Hg	0.05/0.07	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*
Ni	20/4.0	10.8	26.4	3.9	24.0	5.5	34.0
Pb	7.2/1.2	*0.5*	2.8	*0.5*	1.3	*0.5*	2.9
Se	3.0/3.0	2.5	*0.5*	*0.5*	11.2	1.5	1.4
Tl	0.2/0.2	*0.025*	*0.025*	*0.025*	*0.025*	*0.025*	*0.025*

Notes: * EQS for Cadmium (Filtered):			**Legend**	
Calcareous-dolomitic	0.25	[μg/L]		
Metallogenic	0.09	[μg/L]	(grey shading)	Background value > EQS
Bogs/riverside meadows	0.25	[μg/L]		
Saliniferous	0.15	[μg/L]	P90	90th percentile
Sandy-clayey	0.25	[μg/L]	*italic*	Value below detection limit
Siliceous	0.25	[μg/L]		

Geochemically sensitive areas, in terms of metals in the filtered phase, are especially located in the metallogenic and saliniferous riverine landscapes, but also in the siliceous and calcareous-dolomitic riverine landscape (for silver and cadmium). As can be seen in Figure 1, from the ARLs and the geological setting of Saxony-Anhalt, the metallogenic and saliniferous riverine landscapes can be found, more or less, in only the Harz Mountains and their surroundings. Ag, Ni, Pb, and As are directly related to the geochemical characteristics of the metallogenic RL type. Rivers coming down from the mountains may transport these metals into the flat areas, where siliceous and calcareous-dolomitic riverine landscapes are located. Further, the more or less widespread increase of cadmium concentration was already stated in the Geochemical Mapping of Germany [41] and represents a ubiquitous problem.

The implications of the investigation results for the management of surface water quality lead to the necessity for the application for less stringent quality objectives for the rivers of WBs in the Lopinginan Zechstein group and of the Harz Mountains at the European Commission due to natural geochemical features according to Articles 4 (4) [8] and 4 (5) [9] of the WFD [1]. The approval of less stringent quality objectives has direct implications for the cost of the implementation of the WFD in Saxony-Anhalt. Costs are related in this regard to rehabilitation cost (which can be saved due to natural origin of the increased concentrations), as well as monitoring cost (which can be saved due to the exploitability of the monitoring data of the environmental authority). The developed methodology has a significant importance for the environmental policy in Saxony-Anhalt, as it provides an acceptable justification approach for the application of WFD exemptions.

5. Conclusions

The results of the investigation allow the determination of RLs with increased background levels for certain metals or metalloids. The influence was classified as having two levels, (a) a significant increase by >50% compared to the mean values of the geogenic background concentrations (P90), as per RL (indicated below in normal writing style); and (b) moderate increase by >25% in comparison to the RL mean values, which are indicated in *italic* writing style below:

calcareous-dolomitic riverine landscape:	Al, B, *Ba, Cd*, Co, Cr, Se, U
metallogenic riverine landscape:	*Al*, As, Be, Cd, Co, *Fe*, Mn, Ni, Pb, Zn
bogs and riverside meadows:	Fe, *Mn*, *Mo*
saliniferous riverine landscape:	Ag, As, B, Cr, Cu, Mo, *Ni, Pb*, Se, Ti
sandy-clayey riverine landscape:	Al, Fe, Mn, U
siliceous riverine landscape:	Ag, Be, Cu, Mo, Ni, Pb, V

The results show, as for a metallogenic RL expected, higher background concentrations for a number of metals and metalloids. The spacious distribution of the metallogenic RL covers along the Eastern Harz Mountains, and also along the periphery in the south and southeast of the Harz Mountains due to the existence of the Lopingian Zechstein group, where copper shale occurs naturally. The East Harz Mountains are considered the most important area that will be subject to the application for exemptions in terms of natural geochemical features [50,52] according to Articles 4 (4) [8] and 4 (5) [9] of the WFD [1]. Further, higher levels of geogenic metals are observed in the saliniferous RL, caused by special geochemical conditions in terms of the pH value and the redox potential, which determine the mobility of metals.

In all RLs were observed concentrations of the metals, which are regulated in the surface water ordinance through EQS. The EQS for Ag of 0.02 μg/L was exceeded in all RL types, with the highest values in the saliniferous RL (0.18 μg/L) and the siliceous RL (0.14 μg/L). The largest number of exceeded values was determined in metallogenic and saliniferous RLs, with a focus on As. The EQS for As (1.0 μg/L) was exceeded in the metallogenic RL by five times, and in the saliniferous RL by 13 times. A similar situation was determined for Se: the EQS (3.0 μg/L) in the saliniferous RL was exceeded nearly four times. Taking into consideration the geochemical composition of the soil, these values reflect the increased geogenic background of the geological setting. Further, the results indicate that some RLs are observed as having higher background concentrations for uranium (compared to the average levels in Birke et al. [41]), a conclusion that complies with the results in Schneider et al. [52], which proposed the copper shale areas as a source for uranium.

The approach of using the 50th and 90th percentiles for the data evaluation is comparable to Birke et al. [41], and also applied in some other cases documented in the literature. Some authors use the 10th percentiles to exclude the anthropogenic influences; these approaches do not consider a data pre-selection. The developed methodology, including data pre-selection, allows the use of the existing database of the competent authorities, and was validated for Saxony-Anhalt.

The developed methodology was considered to be sufficient for the calculation of geogenic background values and recently adopted in the Draft Technical Guidance "Consideration of natural background concentrations for the assessment of exceedances of EQS for non-synthetic pollutants" by the Working Group of the Federal States on Water—Committee for Surface and Coastal Waters (LAWA-AO), a policy document for the implementation of the WFD. Further, the methodology was considered an acceptably justified approach for the application of WFD exemptions. The guideline is intended as support for the implementation of the Surface Water Directive of Germany (OGewV) [45].

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Conflicts of Interest: The authors declare no conflict of interest.

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