Joint recording of contamination status, multi-element dynamics, and source identification on a sub-catchment scale: The example Lahn River (Germany)

Jens Hahn [a,b,*], Virginia Zils [b], Laura Berresheim [b]

[a] Federal Institute of Hydrology, Am Mainzer Tor 1, 56068 Koblenz, Germany
[b] Department of Geography, Institute for Integrated Natural Sciences, University of Koblenz-Landau, Universitätsstr. 1, 56070 Koblenz, Germany

HIGHLIGHTS

- Enrichment, mobility, and sources of trace elements were studied simultaneously.
- Historic mining sites act as sources of contaminants for the lower Lahn River.
- Dissolved trace metals are mainly introduced into the Lahn River by two tributaries.
- Cd, Co, Mn, Ni, and Zn are enriched in suspended matter and the dissolved phase.
- Pb is enriched in suspended matter and the particulate fraction.

GRAPHICAL ABSTRACT
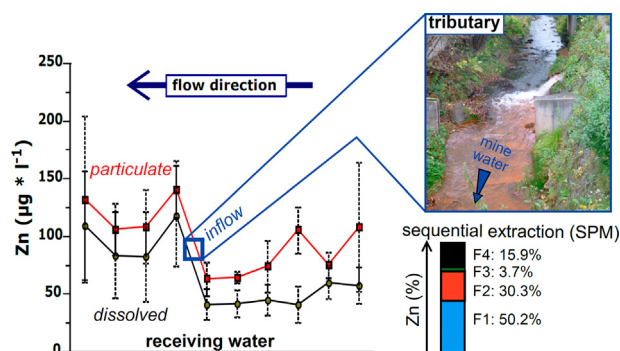
ARTICLE INFO

ABSTRACT

Investigations on the enrichment level, binding dynamics, and source identification of contaminants are important objectives of environmental research into surface waters, but are often carried out independently of each other. To simultaneously address these issues an investigative approach is presented that combines multi-element analyses of water and suspended particulate matter (SPM) and is applied on the scale of a sub-catchment, using the Lahn River (Germany) as an example. Analyses of water and SPM comprised phosphorus (P), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd), lead (Pb), and uranium (U). For the dissolved phase, the investigations additionally included nitrogen compounds (NH_4, NO_3) and dissolved organic carbon (DOC). SPM of the Lahn showed increased average concentrations of Zn (2.13 g kg^{-1}), Cd (4.01 mg kg^{-1}), and Pb (160 mg kg^{-1}). The water phase sampled from points along the length of the Lahn showed significant spatial differences in the dissolved concentrations of Mn (15.7–98.4 µg l^{-1}), Co (0.08–0.66 µg l^{-1}), Ni (0.75–4.69 µg l^{-1}), Zn (19.9–187 µg l^{-1}), and Cd (0.01–0.18 µg l^{-1}), which could be attributed to the inflow of two tributaries draining historic mining areas. The study emphasizes the importance of mine waters during low water periods and proves that such sources can differently affect the SPM quality and the dissolved concentrations of their receiving waters.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

The concentrations of potential nutrients and pollutants significantly influence the chemical quality of running waters. In recent years, an improvement in water quality has been achieved in many Central

* Corresponding author at: Federal Institute of Hydrology, Am Mainzer Tor 1, 56068 Koblenz, Germany.
E-mail address: jens.hahn@bafg.de (J. Hahn).

European rivers through the reduction of substance emissions (Delpla et al., 2009; EEA, 2010). This has mainly been achieved by regulating point sources such as urban sewage treatment plants or industrial wastewater (Mohaupt et al., 2001). According to the European Water Framework Directive, EU Member States are obliged to achieve a good chemical status in their waters until 2027. For surface waters in Germany, this is implemented by the Surface Water Ordinance (OGewV, 2016). The good chemical status of water bodies is determined by means of environmental quality standards for "priority substances", i.e. selected substances with special environmental relevance. Whether this goal can be achieved for the majority of the watercourses is, however, questionable at present. Inputs from remaining point sources and from diffuse sources that are still difficult to regulate are partly sufficient to impair water quality at present (Romero et al., 2016). Seasonal variations of water quality could also be influenced by the effects of climate change, which is predicted to be connected with an increasing frequency of low discharge and flash floods in the summer months for large parts of Central Europe (IPCC, 2014; Sedlmeier et al., 2018). Low water levels can be associated with a temporary increase of element concentrations, which results from a decreasing dilution (Cánovas et al., 2018), an increasing baseflow (Dragun et al., 2011), or the enrichment of element rich fine particles in the water column (Zerling et al., 2006). Essentially, during low water levels the proportion of water released by substance sources with continuous emission rates throughout the year can increase significantly and thus influence the chemistry of their receiving water (Nordstrom, 2009). Flash flood events, in contrast, can be connected with a reactivation of temporarily inactive contaminant sources (Foulds et al., 2014; Runkel et al., 2016).

Since an increasing intensity of hydrological extremes can lead to more frequent occurrence of negative effects on chemical water quality, the identification of problematic substances and their sources is of increasing importance. Substances do not always enter larger watercourses from direct sources, but are often introduced through smaller tributaries. Such secondary sources are not necessarily subject to official monitoring programs. In order to explain spatial concentration changes in a river it is, therefore, necessary to extend hydrochemical investigations to catchment or sub-catchment areas (Froger et al., 2018).

Suspended particulate matter (SPM) or water samples are often used to investigate the contamination status, pollutant dynamics or pollutant sources of surface waters (Gozzard et al., 2011; Moraetis et al., 2011; Resongles et al., 2015). Particularly for the collection of SPM different methods are used in hydrochemical research. Larger amounts of SPM can be obtained by centrifugation or particle traps (Masson et al., 2018; Keßler et al., 2020). Filtration techniques in particular are suitable for the simultaneous analysis of both the particle-bound quantities of trace metal and metalloid elements (TMM) and the SPM concentration of the water phase. However, relatively small sample quantities are obtained, which reduces the scope of the possible analyses (Ödman et al., 1999, 2006). Another method to determine particulate or total TMM concentrations of the water phase is the in-bottle digestion method (Garbarino and Hoffman, 1999). Due to its ease of use, in-bottle digestion allows the generation of high sample numbers, but the analytical capabilities are limited to the TMM content. A special feature of this study is the design of the sampling campaign, which allows the detailed analysis of SPM quality and a separate consideration of dissolved and total concentrations of the water phase at the sub-catchment level. Based on this, results of the contamination status, element dynamics, and source identification are provided for a relatively wide range of substances (metals, metalloids, and nitrogen compounds).

The investigations were carried out exemplarily in the sub-catchment area of the lower Lahn River (Germany). This river crosses a historic mining region and is characterized by increased concentrations of various metals and nutrients, without the sources of these substances having been identified exactly so far. In 2018, the Lahn was subject to a pronounced low water period, so that the results of the investigation reflect an extreme situation that may occur more frequently in the future. The objectives of the study were (i) to simultaneously record the contents of trace metal(oid)s, P, and N-compounds in SPM and in the water phase, (ii) to analyze the binding dynamics of potential pollutants, and (iii) to investigate the role of tributaries as sources of substances in the lower Lahn basin.

2. Material and methods

2.1. Study area

The study area is located within the lower Lahn basin (Germany) between the cities of Diez and Lahnstein. The regional climate has an average annual temperature of 9.7 °C and an average annual precipitation of 798 mm (DLR, 2019). The Lahn River is largely canalized and impounded by 8 weirs and locks within the study area. The tributaries are located in steep V-shaped valleys, with forestry being the dominant form of land use (Supplementary material, Fig. S1). The state of Rhineland-Palatinate regularly collects discharge data for the Lahn, Gelbach, Dörsbach, and Mühlbach rivers (Supplementary material, Fig. S2). The contribution of the tributaries to the discharge of the Lahn follows the order Gelbach > Dörsbach, Mühlbach >> Emsbach >> other tributaries.

Geology is dominated by Devonian rocks (shale, quartzite, greywacke, and siltstone) (Supplementary material, Fig. S3). These Devonian rocks are characterized by the occurrence of Variscan mineralizations, especially between the towns of Laurenburg and Lahnstein, often containing sulphidic minerals of Pb and Zn (Jochum, 2000). Metallurgical activities were carried out throughout the whole study area during the Middle Ages and in Modern Times, with the Holzappel, Bad Ems, and Friedrichssegen mines being the most important (Wieber, 1994) (Fig. 1). The metallurgical era came to an end after the last mines were closed in the first half of the 20th century. The amount of raw ore produced in the Holzappel mine is estimated at 3.95 MT, the total amount of raw ore produced in the Bad Ems district, including Friedrichssegen, is estimated at 10.5 MT (Bode, 1983; Scheid, 1994). The last processing plant (Bad Ems, Silberau) was shut down in 1959. As a legacy of mining, the soils, floodplains, and sediments of the lower Lahn Valley are partially contaminated with Zn and Pb (Lenz, 1986; Hahn et al., 2016).

2.2. Sampling design

The main selection criterion of the study area was the combination of a largely channelized river and a catchment with a small-scale changing land use. Due to the heterogeneity of the catchment area, the tributaries should differ in their substance profile. In contrast, the channeled, slowly flowing water of the Lahn River facilitates the tracing of individual substance sources. Sampling was performed between August and November 2018. Since the beginning of June, the Lahn was subject to a particularly low discharge period, which was characterized by the nearly complete absence of summer rainfall events and lasted until the beginning of December 2018 (Supplementary material, Fig. S2). The sampling strategy was to investigate SPM and water samples from the longitudinal course of the Lahn at ten comparable locations: Lahnstein (LS), Friedrichssegen (FR), Miellen (Mi), Nievern (Ni), Bad Ems (BE), Dausenau (DS), Nassau (NS), Obernhof, (OH), Kalkofen (KA), and Laurenburg (LB) (Fig. 1). The ten most important tributaries of the study area were included in the investigations in order to record the resulting substance inputs into the Lahn.

Multi-element analyses were carried out to ensure a comprehensive joint recording of substance dynamics and sources, and included phosphorus (P), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd), lead (Pb), and uranium (U). Nitrogen compounds were analyzed in form of ammonium (NH_4) and nitrate (NO_3).
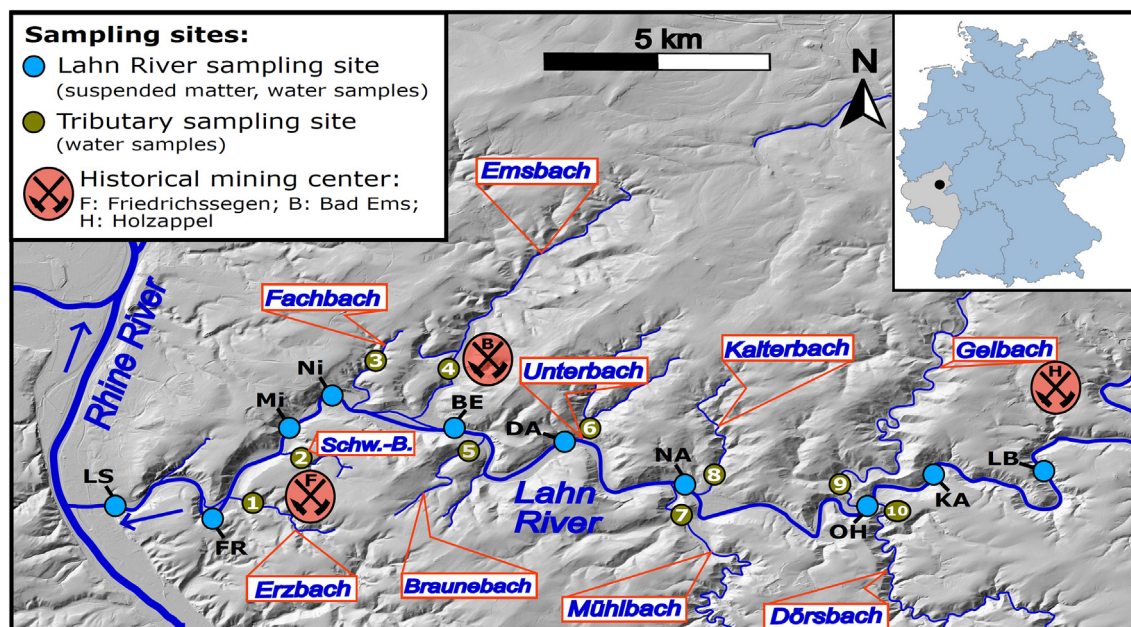
Fig. 1. Area of investigation and location of the sampling sites (map based on LVermGeoRP (Landesamt für Vermessung und Geobasisinformation Rheinland-Pfalz), 2020). The numbers represent the sampling sites of the tributaries and can be attributed as follows: 1: Erzbach, 2: Schweizertalbach, 3: Fachbach, 4: Emsbach, 5: Braunebach, 6: Unterbach, 7: Mühlbach, 8: Kalterbach, 9: Gelbach, 10: Dörsbach.

2.3. Field- and laboratory work

2.3.1. Suspended matter samples

The SPM of the Lahn River was collected in custom-made PVC-samplers, which were fixed at a depth of 1.0–1.5 m below the water level. All samplers were emptied every two weeks. To obtain sufficient sample quantities the samples were combined into monthly mixed samples ($n = 2$ each sampling site). All samples were air-dried, ground, and homogenized in a porcelain mortar before analysis.

For grain size analysis, the SPM samples were mixed with water and a dispersing agent ($Na_4P_2O_7$) and sonicated for 10 min. The grain size distribution was determined by laser diffractometry (LS 200, Beckman Coulter). The analysis was performed on triplicates of each sample within a measuring range from <2 mm to >0.3 μm. The results were divided into the grain size fractions coarse sand (2000–630 μm), medium sand (630–200 μm), fine sand (200–63 μm), coarse silt (63–20 μm), medium silt (20–6.3 μm), fine silt (6.3–2 μm), and clay (<2 μm).

After drying (16 h at 105 °C) and grinding the samples, the concentrations of organic carbon (C_{org}) and total nitrogen (N_t) were analyzed by a C/N analyzer (vario EL cube, Elementar).

The binding behavior of TMM in the SPM samples was analyzed using the revised BCR sequential extraction procedure according to Rauret et al. (1999). Within this procedure, a sample is extracted by a sequence of different extracting agents (Supplementary material, Table S1), in order to divide the total concentration of TMM into an exchangeable (F1), a reducible (F2), an oxidizable (F3), and a residual (F4) fraction. For this analysis, all vessels were leached in 5 mol l^{-1} HNO_3 prior to use. 1 g of each sample was subjected to four consecutive extractions. After each extraction step the extracts were separated from the samples by centrifugation (3000 g, 20 min). To avoid contamination, the samples were shaken in ultrapure water for 15 min and centrifuged again between each extraction. The following extraction agents were used to obtain the binding fractions: exchangeable: 0.11 mol l^{-1} acetic acid ($C_2H_4O_2$); reducible: 0.5 mol l^{-1} hydroxylammonium chloride (($NH_3OH)Cl$); oxidizable: ammonium acetate ($C_2H_7NO_2$) (after prior reaction with 8.8 mol l^{-1} hydrogen peroxide [H_2O_2]). All extractions were performed by shaking the samples for 16 h. For the extraction of the residual fraction the samples were heated in aqua regia for 2 h. All

extracts were diluted with ultrapure water. The concentrations of V, Cr, Mn, Fe, Ni, Cu, Zn, and Pb were determined by ICP-OES (Optima 8300, Perkin Elmer). The concentrations of P, Co, As, Cd, and U were analyzed by triple quadrupole ICP-MS (8800 series, Agilent Technologies). The analytical precision was controlled by certified reference materials (Metranal River Sed. 1, Nist 1646a).

2.3.2. Water samples

At each of the 20 sampling locations water sampling and field measurements were conducted every two weeks for a four-month period ($n = 8$ each sampling site). Electrical conductivity and pH-values were measured with a portable field-meter (P5, WTW). All containers of water samples were rinsed with acid (5% HNO_3) and ultrapure water before sampling. At each sampling site, two water samples were taken from a water depth of 10 cm. One water sample was filtered to 0.45 μm (minisart NML, cellulose acetate, Sartorius). After filtration, the sample was divided into two aliquots. One aliquot was mixed with 1% HNO_3 for the analysis of element concentrations. The second replica was used to analyze nitrogen compounds and DOC. Since a release of carbon-containing compounds cannot be excluded when organic filter materials are used, the filters were rinsed with sample water before filtration. The potential release of DOC from the filter materials was controlled by multiple blank samples of ultrapure water and proved to be negligible.

The second water samples were filled unfiltered into PE bottles and subjected to an acid in-bottle digestion (Garbarino and Hoffman, 1999) in the laboratory. This was performed to determine the total concentrations of TMM. To the unfiltered samples 3% HNO_3 was added. The samples were heated in an oven at 60 °C for 8 h, vigorously shaken, and filtered to 0.45 μm. All samples were frozen at −18 °C until analysis. To prevent contamination during filtration and in-bottle digestion, the sample series were regularly controlled by blank samples. To detect possible gas losses of TMM concentrations, defined standard solutions were treated by the same procedure. The recovery for all TMM was >90%.

Since the TMM concentrations determined by in-bottle digestion are not able to completely dissolve very strongly bound TMM (e.g. bound in the crystal structure of mineral particles), they do not fully correspond

to the total concentrations of the water phase. For reasons of readability, however, the term "total content" is used below. To avoid contamination during TMM analysis, sub-boiled HNO_3 was used as reagent for water samples and standard solutions. Samples with high concentrations were diluted with ultrapure water to be within the calibration ranges. All element concentrations of the water samples were determined by triple quadruple ICP-MS (8800 series, Agilent Technologies). The analytical precision was controlled by the use of certified reference materials (SPS-SW1, SPS-SW2, TMDA-64.3). As criterion of acceptance a recovery ≤10% was selected.

The concentrations of NH_4 and NO_3 of the filtered water samples were determined by means of a continuous flow analyzer (AutoAnalyst 3, Seal Analytical/Bran+Luebbe).

The concentrations of DOC were determined with a TOC-analyzer (DimaTOC 2000, Dimatec).

2.3.3. Statistics

Descriptive statistics and statistical data analyses were performed using IBM SPSS Statistics 26. The enrichment factor (EF) was used to estimate anthropogenic impacts on TMM concentrations of the SPM samples. To exclude the impact of sample inhomogeinity, the EF was normalized by the concentration of Al. The element-specific EF were calculated (Dung et al., 2013):

$EF = (M/Al)_S/(M/Al)_r$ where $(M/Al)_S$ is the TMM/Al ratio of SPM divided by $(M/Al)_r$, which is the element-specific ratio to Al in European stream sediments according to Salminen (2005). Reference values were (mg kg^{-1}): Al = 54,500, P = 611, V = 29, Cr = 21, Mn = 452, Fe = 19,700, Co = 8, Ni = 16, Cu = 14, Zn = 60, As = 6, Cd = 0.28, Pb = 14, and U = 2.

Sample specific element concentrations were evaluated according to the following scheme: EF ≤1: no enrichment; 1 < EF ≤3: minor enrichment; 3 < EF ≤5: moderate enrichment; 5 < EF ≤10: moderately severe enrichment; 10 < EF ≤25: severe enrichment, 25 < EF ≤50: very severe enrichment; EF > 50: extremely severe enrichment.

The index of geo-accumulation (I_{geo}) was calculated to evaluate the intensity of TMM accumulation according to Mueller (1986), following the equation:

$$I_{geo} = log_2\left(\frac{M_s}{M_r * 1.5}\right)$$

where M_s is the TMM concentration of a sample and M_r is the element-specific baseline value for European stream sediments (Salminen, 2005) (Supplementary material, Table S2). To evaluate the contamination state, the I_{geo} of each element and sample was evaluated according to the following classification: I_{geo} < 0: uncontaminated (class 0); I_{geo} 0–1: uncontaminated to moderately contaminated (class 1); I_{geo} 1–2: moderately contaminated (class 2); I_{geo} 2–3: moderately to strong contaminated (class 3); I_{geo} 3–4: heavily contaminated (class 4); I_{geo} 4–5: heavily to extremely contaminated (class 5); I_{geo} > 5: extremely contaminated (class 6).

To combine all investigated contaminants in one contamination index, the pollution load index (PLI) was calculated according to Rinklebe et al. (2019):

$PLI = (CF_1 * CF_2 * ... * CD_n)^{1/n}$ where CF_1, CF_2, CF_n are CF of elements 1, 2, …, n. The contamination load was classified: PLI <0: unpolluted; 0 < PLI ≤1: baseline level; 1 < PLI ≤10: polluted; 10 < PLI <100: highly polluted.

All data collected from water samples were controlled for normal distribution using the Shapiro-Wilk-Test. For the vast majority of the studied elements and parameters a non-normal distribution was observed. Therefore, non-parametric tests were selected to conduct analyses. In order to investigate the role of the Lahn tributaries as sources of inorganic nutrients and pollutants, the data collected in the longitudinal course of the Lahn were checked for site-specific differences using the Kruskal-Wallis H test. The dataset was then analyzed by means of Dunn-Bonferroni post hoc test. This was conducted, in a first step, for the data of sampling sites of the longitudinal course of the Lahn and, in a second step, for all data of the Lahn and of the tributaries.

In order to identify commonalities in the dynamics of the investigated elements, the dataset of the Lahn was subsequently analyzed by Principal Component Analysis (PCA). The suitability of the data for PCA was controlled by Kaiser-Meyer-Olkin and Bartlett's sphericity tests. As axis rotation an orthogonal varimax rotation was applied. Finally an analysis of three principal components was selected.

3. Results

3.1. Suspended particulate matter

The particle size distribution of the SPM samples showed very low amounts of coarse sand (0.0–3.4%) and medium sand (0.6–15.3%) at all sampling sites, while fine sand (10.0–23.0%) had slightly higher percentages (Table 1). The grain sizes of nearly all samples were dominated by coarse silt (18.9–35.7%) and medium silt (18.9–32.3%), while the proportions of the fine silt (15.3–25.0%) and clay (6.0–15.0%) fractions were mostly lower. All samples were characterized by relatively high concentrations and a relatively low variability of C_{org} (4.4–7.7%) and N_t (0.36–0.65%).

The mean concentrations of trace metals and metalloids (TMM) and the EF of the SPM showed at least slight enrichments for all elements studied (Table 2). EF and I_{geo} of P, Mn, Ni, and Cu correspond to moderate enrichments. Both indices indicate severe enrichment and contamination for Cd and Pb, while the concentrations of Zn must be considered very severe enriched and extremely contaminated. The PLI of the SPM resulted in a mean value of 2.36 ± 0.37. The SPM of the lower Lahn are accordingly considered as polluted. However, Zn was the only element that exceeded the threshold values for SPM according to the European Water Framework Directive (OGewV, 2016). At the same time, Zn was the only element that showed a gradient of the EF in the longitudinal course of the Lahn by continuously achieving high values downstream of the sampling site BE. In comparison, the median value of the EF of Zn in the section LB–BE increases from 29.9 to 45.9 in the section Ni–LS (Supplementary material, Table S3). The other highly enriched elements such as Cd and Pb reached a high EF already upriver BE without showing a clear gradient (Fig. 2).

Looking at the proportions of TMM in different binding fractions of the sequential extraction procedure, over 20% was found on average in the exchangeable (F1) fraction of Mn, Co, Zn, and Cd (Table 2). For the same elements, the reducible (F2) fraction reached the highest or second highest percentage. For V, Cr, Fe, Cu, As, and U the highest proportions on total concentrations were found for the residual (F4) fraction. As the only element, Pb showed by far the highest proportions in the reducible (F2) fraction (70.1%). Ni showed highest amounts in the residual (F4) fraction, but reached percentages >10% within all other fractions.

Table 1
Mean percentages of the grain size fractions and the percentages of organic carbon (C_{org}) and total nitrogen (N_t) of SPM of the lower Lahn River ($n = 18$).

Grain size fraction (μm)							C_{org} (%)	N_t (%)
2000–630	630–200	200–63	63–20	20–6.3	6.3–2	<2		
0.8 ± 1.1	5.6 ± 5.4	14.8 ± 3.8	24.4 ± 4.6	25.9 ± 4.5	19.0 ± 3.3	9.5 ± 2.5	5.87 ± 0.9	0.52 ± 0.1

Table 2

Statistics of the total concentrations of TMM and P (Fe, Mn, and Zn in g kg^{-1}, other elements in mg kg^{-1}) (SD: standard deviation; Min: minimum value; Max: maximum value; p: percentile), the mean values of enrichment factors (EF) and I$_{geo}$, and the mean percentage of the binding fractions (F1: exchangeable, F2: reducible, F3: oxidizable, F4: residual) of TMM total concentrations of SPM of the lower Lahn River ($n = 19$).

	P	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb	U
Min	897	18.3	20.3	1.64	14.3	13.9	55.8	22.8	0.90	4.00	1.67	100	0.34
25th p.	1634	40.0	48.2	2.82	33.2	18.4	62.5	47.7	1.58	7.23	3.34	131	0.64
50th p.	1812	41.4	54.7	3.18	35.2	20.2	65.8	52.7	2.07	7.71	4.06	143	0.67
75th p.	1952	44.2	55.7	3.58	36.1	26.1	80.1	54.7	2.64	11.9	4.87	187	0.69
Max	2278	47.6	59.6	5.26	38.9	30.2	120	67.4	3.24	17.3	5.83	285	0.74
Mean	1766	39.5	49.9	3.22	32.5	21.9	74.6	50.3	2.13	9.64	4.01	160	0.64
SD	370	8.33	11.0	0.82	6.97	4.74	19.8	9.59	0.63	3.86	1.10	49.1	0.11
EF	3.03	1.45	2.53	7.54	1.75	2.82	4.87	3.79	37.2	1.63	14.7	12.0	0.34
SD	0.79	0.39	0.70	2.05	0.46	0.54	1.15	0.29	10.2	0.54	4.00	3.59	0.08
I$_{geo}$	1.41	0.39	0.89	2.83	0.83	1.29	2.22	1.89	5.11	0.39	3.67	3.39	0.00
SD	0.62	0.50	0.32	0.38	0.38	0.47	0.43	0.32	0.47	0.50	0.59	0.50	0.00
F1 (%)	–	0.74	0.14	47.7	0.31	22.7	11.5	1.74	49.2	4.55	42.2	0.42	1.48
SD		0.58	0.10	12.1	0.66	15.3	0.80	13.1	3.61	10.8	0.87	0.81
F2 (%)	–	22.6	8.77	35.7	23.8	48.8	19.1	16.7	29.3	23.5	44.5	70.1	14.0
SD		8.99	3.51	15.3	9.35	17.6	6.20	3.62	7.06	12.7	9.20	17.4	6.53
F3 (%)	–	9.27	20.7	1.92	2.61	10.0	10.4	24.5	3.58	10.6	7.83	4.18	16.3
SD		4.57	10.5	0.74	1.42	2.53	3.16	11.4	1.21	3.76	3.60	1.08	6.57
F4 (%)	–	67.4	70.4	14.6	73.3	18.4	59.0	56.9	18.0	61.3	5.48	25.3	68.2
SD		13.5	13.9	11.5	10.5	11.9	10.3	13.2	19.8	17.5	4.21	18.2	13.4

3.2. Hydrochemical comparison of the Lahn River and its tributaries

The mean dissolved concentrations of Cr, Ni, Cd, Pb, and NO$_3$ of the Lahn complied with the threshold values according to OGewV (2016). The coefficients of variance (CV) of Co, Cu, Zn, Cd, Pb, and NH$_4$ with values >50% indicated comparatively increased spatial or temporal variations of the concentrations (Table 3). The tributaries showed in particular high CVs for Mn, Co, Zn, and Cd due to extremely high concentrations of the tributaries 1 (Erzbach) and 4 (Emsbach). The percentage of the dissolved concentrations to the total TMM concentrations determined by in-bottle digestion varied by element. Especially Fe and Pb achieved low percentages in the dissolved fraction. Also, the dissolved percentages of Cr, Mn, Co, and Cd were close or below 50% of total contents. In contrast, dissolved P, V, Ni, Cu, Zn, As, and U continuously exceeded 50% of the total concentrations.

The pH value of the Lahn was neutral to slightly alkaline with variations between pH 6.9–8.6 (Supplementary material, Table S.8). Depending on the tributaries, variations were found within a weakly alkaline pH range (pH 7.5–8.6). The mean electrical conductivity (492–671 µS cm^{-1}) of the Lahn was higher than for the tributaries. These, on the

other hand, were characterized by distinct site-specific variations, indicating different loads of major cations and anions (Mc Cleskey et al., 2012). As a result, the variability of the electrical conductivity of the tributaries (167–772 µS cm^{-1}) was significantly higher than for the Lahn.

3.3. Potential nutrients and pollutants in the longitudinal course of the Lahn River

While the concentrations of N-compounds and DOC were relatively balanced (Supplementary material, Fig. S4), the Kruskal-Wallis H test conducted for the different sampling locations along the longitudinal course of the lower Lahn River indicates the presence of significant spatial differences ($p \leq 0.01$) in the dissolved concentrations of Mn, Co, Ni, Zn, and Cd (Table 4). A comparison of the sampling sites of the Lahn by means of a Dunn-Bonferroni post hoc test shows a significant increase in the dissolved concentrations of Mn, Co, Ni, Zn, and Cd for sampling sites of the section Ni–LS (Fig. 3) downstream of the sampling site BE. The dissolved median concentrations of the downstream sampling section Ni–LS clearly exceeded the median concentrations of the upstream sampling section LB–BE in the case of Mn (93%), Co (79%), Ni (55%), Zn (94%), and Cd (39%) (Supplementary material, Table S4).

In order to correlate possible effects of tributaries on the water quality of the Lahn, a second post hoc test was conducted comparing the dissolved concentrations in the Lahn and its tributaries (Supplementary material, Fig. S5). At the tributaries 1 (Erzbach) and 4 (Emsbach) significant differences to all other sampling locations were found for the dissolved concentrations of Mn, Co, Ni, Zn, and Cd, the same elements which showed variations in concentration over the longitudinal course of the Lahn (Fig. 4). These elements had dissolved mean concentrations in tributary 1 which exceeded the other sampling sites by the factors 16 (Ni) to 350(Mn), the tributary 4 values exceeded other sampling sites by the factors 3.3(Ni) to 99.8(Cd). The concentrations of dissolved Pb of tributary 1 and 4 were also significantly different from the other sampling sites. However, the other site's mean values were only exceeded by the factors 4.0–10.

For the total concentrations of the water phase, the Kruskal-Wallis H test for the longitudinal course of the Lahn showed significant differences for Mn, Fe, Co, Zn, Cd, and Pb. However, compared to the dissolved concentrations, these were less clearly expressed in differences between the sections LB–BE and Ni–LS. The median values of the total concentrations of the section Ni–LS exceeded the upstream section LB–BE in the case of Co (60%), Mn (47%), Ni (48%), Zn (55%), and Cd (12%).
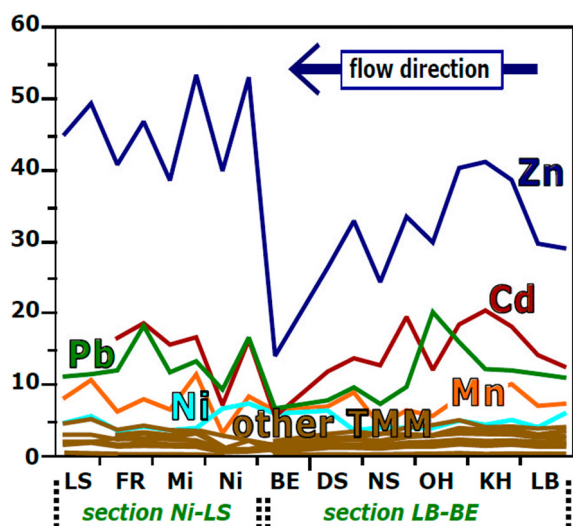

Fig. 2. The site-specific EF in the longitudinal course of the lower Lahn River.

Table 3
Statistics of the dissolved concentrations of TMM (µg l^{-1}), nitrogen compounds, and DOC (mg l^{-1}) of the lower Lahn River ($n = 80$) and its tributaries (n = 80) (SD: standard deviation; Min: minimum value; Max: maximum value; CV: coefficient of variation; D/T(%): mean percentage of the dissolved fraction on the total concentration).

Element		P	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb	U	NH$_4$	NO$_3$	DOC
Lahn River	Min	47.8	0.36	0.14	15.7	19.0	0.08	0.75	0.81	19.9	0.28	0.01	0.07	0.14	0.04	0.98	21.5
	25th p.	91.7	0.81	0.24	25.8	28.4	0.16	1.52	1.42	44.0	0.48	0.03	0.15	0.28	0.12	8.07	33.7
	50th p.	108	1.07	0.28	35.1	38.9	0.21	1.71	1.63	57.2	0.60	0.04	0.20	0.35	0.19	9.82	37.5
	75th p.	115	1.46	0.32	51.6	49.5	0.28	2.13	1.86	82.2	0.72	0.05	0.31	0.41	0.25	11.3	41.6
	Max	154	2.13	0.83	98.4	96.8	0.66	4.69	4.91	187	1.53	0.18	1.56	0.52	0.94	13.3	53.8
	Mean	103	1.16	0.30	39.6	42.9	0.24	1.89	1.77	67.9	0.60	0.04	0.30	0.34	0.21	9.25	37.7
	SD	25.0	0.43	0.11	18.8	19.0	0.13	0.69	0.79	37.6	0.21	0.03	0.29	0.09	0.14	2.47	5.83
	CV (%)	24.2	37.2	36.1	47.5	44.3	53.0	36.4	44.7	55.4	34.1	59.0	97.3	25.8	66.5	26.7	15.5
	D/T (%)	65.5	73.0	41.1	54.1	17.3	54.1	72.9	68.2	70.0	74.5	45.5	17.0	81.7	–	–	–
	SD	16.5	21.9	19.9	21.4	14.4	21.6	19.8	21.9	37.7	18.0	18.9	15.0	17.1	–	–	–
Tributaries	Min	3.82	0.00	0.07	1.81	6.26	0.01	0.17	0.34	4.67	0.04	0.00	0.07	0.01	0.01	0.25	13.8
	25th p.	11.7	0.12	0.14	4.67	24.0	0.03	0.35	0.76	11.8	0.24	0.01	0.12	0.14	0.07	5.95	25.1
	50th p.	29.6	0.20	0.21	9.30	32.2	0.06	0.76	1.11	21.7	0.29	0.02	0.21	0.22	0.13	7.47	30.0
	75th p.	90.0	0.34	0.31	17.7	54.4	0.14	1.47	1.78	46.1	0.44	0.09	0.57	0.48	0.26	10.7	36.8
	Max	418	1.54	0.97	1089	151	20.4	34.3	8.16	11,038	0.73	14.4	6.58	1.75	1.56	34.5	50.8
	Mean	69.4	0.29	0.24	115	43.8	1.89	3.84	1.66	1290	0.33	1.72	0.94	0.44	0.22	9.68	31.5
	SD	89.2	0.30	0.14	276	29.2	5.18	8.63	1.57	2889	0.15	3.88	1.58	0.51	0.27	8.20	9.94
	CV (%)	129	102	58.7	240	66.7	274	225	94.8	224	44.5	225	168	116	120	84.8	31.5

Especially at site OH the total concentrations of Mn, Fe, Co, Cd, and Pb differed significantly from numerous other sampling sites (Fig. 3).

The PCA of the dissolved concentrations measured at all stations of the lower Lahn conducted for 3 principal components explained 63.1% of the total variance (Fig. 5). The first component explained from 78% to 93% of the variations of Mn, Co, Ni, Zn, and Cd. A second group of similar controlled elements were P, V, As, U, and DOC, being explained from 57% to 83% by component 2. Component 3 summarized 57% to 79% of the variance of Cr, Fe, Cu, and Pb. Variations of NO$_3$ and NH$_4$ were not insightfully explained by these components (Supplementary material, Table S5).

The PCA of the total TMM and P concentrations explained 87.5% of the total variance. Component 1 summarized Mn, Fe, Co, Zn, Cd, and Pb and explained from 71% to 91% of their variations. The second component grouped P, V, Ni, As, and U, being explained from 63% to 91%. Component 3 summarized Cr and Cu and explained 69% and 90% of their variations, respectively.

4. Discussion

4.1. Solid phase

The reported enrichments of Ni, Cu, Zn, Cd, and Pb within the study area are consistent with the results of previous studies. Wieber (1994) and Hauenstein and Hutzler-Gardt (1996) documented strongly elevated concentrations of Zn, Cd, and Pb in soils near former mining areas in Bad Ems, Friedrichssegen, and Holzappel. Downstream of these sites, enrichments of Cu, Zn, As, Cd, and Pb in alluvial soils were reported by Hahn et al. (2016), while Schroeder et al. (2017) recorded enrichments of Cr, Ni, Zn, As, Cd, and Pb in oxbow sediments. This supports the assumption that elements released by historical mining and ore processing were partially enriched in the river system of the lower Lahn.

The generally low proportions of exchangeable (F1) TMM analyzed by sequential extraction indicate a comparatively strong binding of V, Cu, Pb, and As to SPM. This is in accordance with investigations by Helios Rybicka et al. (2005), Liu et al. (2016), and Javed and Shotyk (2018), who found these elements predominantly bound by the

residual fraction (F4) or exchangeable to a small extent. Since the concentrations of V, Cu, and As can be regarded as slightly, at the most moderately, enriched and since these elements have their highest proportions in the residual (F4) fraction, their harmful effects are likely to be negligible. In the case of Pb, whose concentrations are significantly enriched in SPM (EF: 12.0; I$_{geo}$: 3.4), the intensive binding to particle surfaces described above is of high relevance, since it counteracts a release of dissolved Pb into the water phase and thus reduces the comparably higher risk potential of Pb in SPM.

In contrast, Mn, Co, Zn, and Cd reached relatively high exchangeable (F1) amounts in the SPM samples, which can be explained by the interplay of the typically high mobility of these elements (Alloway, 1999) and partially elevated total concentrations. Due to this high mobility in combination with the high concentrations, negative effects of Zn and Cd on the ecosystem of the lower Lahn are likely. This assumption is supported by the results of the PLI.

Overall, high accumulations of Zn, Cd, and Pb occur across the entire study region. A clear influence of the tributaries on the TMM concentration in SPM is not apparent. This can be explained by the fact that polluted sediments from mining activities partly entered the Lahn directly from the processing and transport stations of the mining companies. However, the EFs show that Zn, Cd, and Pb partially have different sources within the study area. While these elements show clear enrichments already at sampling site KH, which is based on entries from areas of the Holzappel mining district, Zn was enriched to a higher extent downstream of BE. This can be explained by the processing of heap materials from the decommissioned mines around Bad Ems, which were used until 1959 at a site near the Lahn (Seeliger et al., 2009) and may have been a source of contaminated material.

4.2. Water phase (dissolved concentrations)

With the exception of DOC and Zn, the dissolved concentrations of TMM and N-compounds in the lower Lahn were comparable to other rivers of the Central European low mountain ranges or to rivers worldwide (Supplementary material, Table S6). The comparatively high DOC concentrations can be explained by the fact that sampling was limited to

Table 4
Asymptotic significances of the dissolved (dis.) and total (tot.) concentrations of TMM, P, nitrogen compounds, and DOC of the water phase from the longitudinal course of the lower Lahn River analyzed by Kruskal-Wallis H test (p ≤ 0.01 in bold).

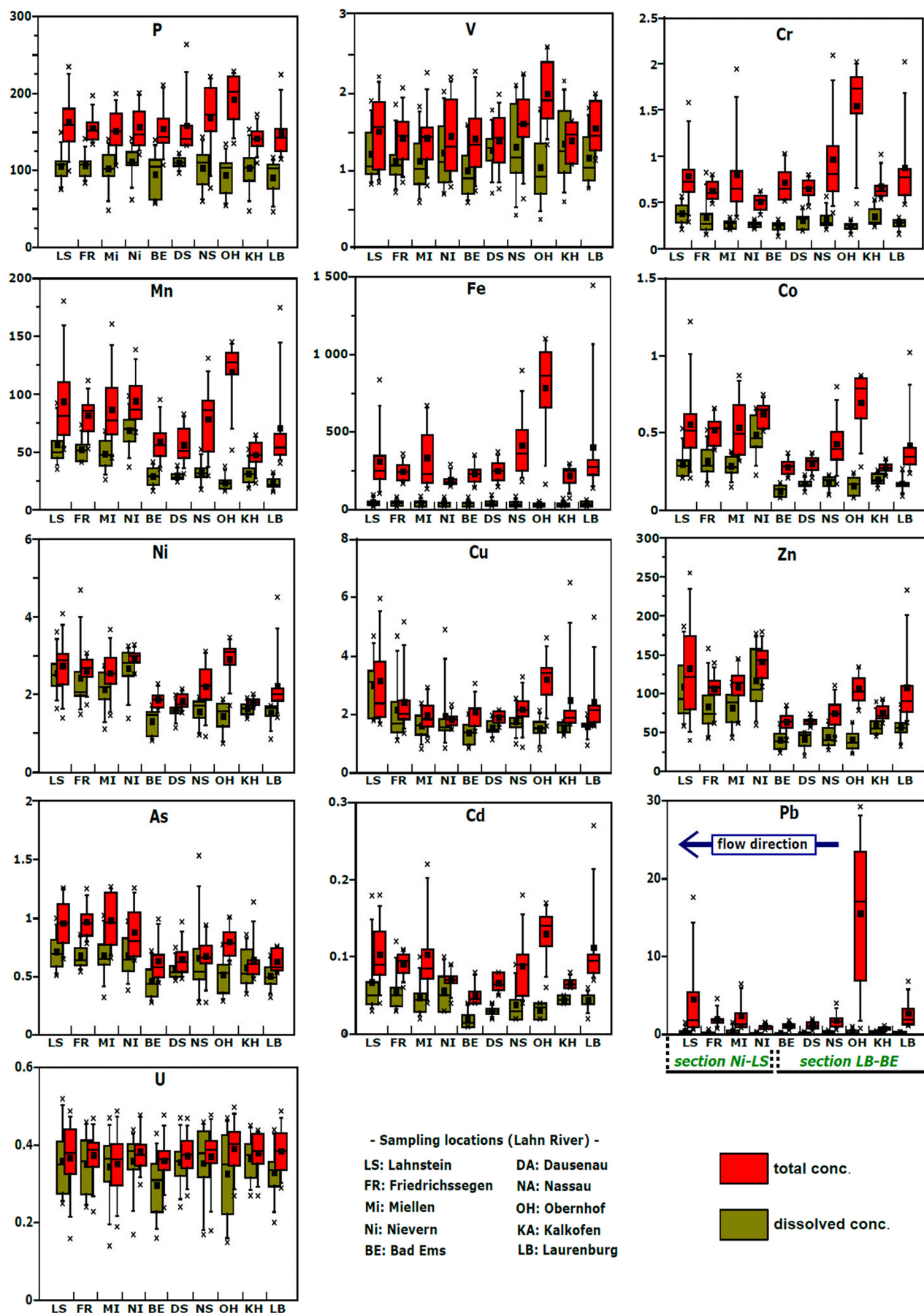		P	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb	U	NO$_3$	NH$_4$	DOC
dis.	0.75	0.83	0.19	**0.00**	0.97	**0.00**	**0.00**	0.09	**0.00**	0.05	**0.00**	0.32	0.90	0.39	0.64	0.44
tot.	0.29	0.30	0.02	**0.01**	**0.01**	**0.01**	**0.01**	0.11	**0.01**	0.25	**0.00**	**0.00**	0.32	–	–	–

Fig. 3. Boxplot diagrams of the dissolved and total concentrations ($\mu g\ l^{-1}$) of TMM and P over the longitudinal course of the lower Lahn River (n = 80).
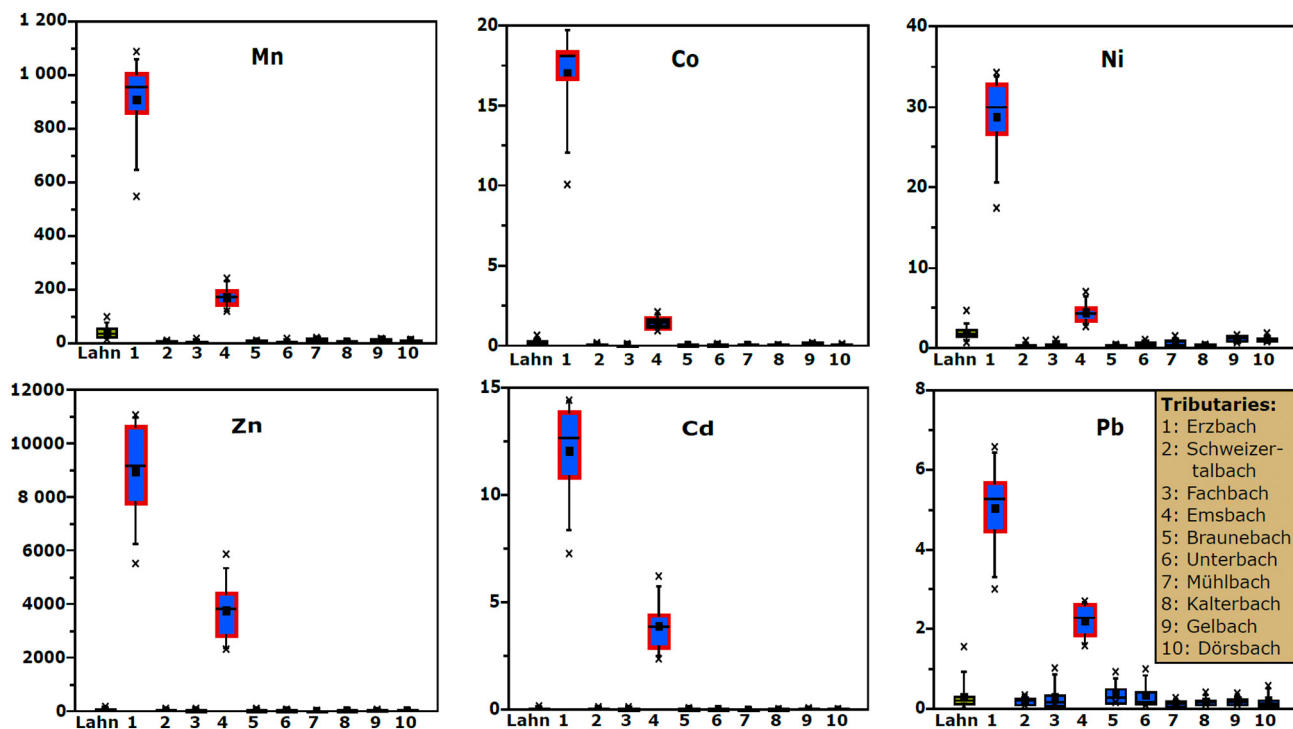
Fig. 4. Comparison of the dissolved concentrations of Mn, Co, Ni, Zn, Cd, and Pb (μg l^{-1}) between all sampling locations of the lower Lahn River (n = 80) and the tributaries 1 to 10 (n = 80). Boxes in red are significant different to the other boxes.

the late summer months while DOC can be significantly lower in other seasons. Although the elevated Zn concentrations are higher than in many other rivers (Gaillardet et al., 2003; Elbaz-Poulichet et al., 2005; Xiao et al., 2019), they can be significantly exceeded in watercourses more strongly influenced by mining (Olías et al., 2004).

With regard to the longitudinal course of the Lahn, the most striking characteristic is the increasing concentration of dissolved Mn, Co, Ni, Zn, and Cd. This is of particular importance since, with the exception of Zn, these gradients do not appear in the TMM concentrations of SPM. The results of the Dunn-Bonferroni post hoc test indicate that these concentration increases can be attributed to the simultaneous input from the tributaries 1 (Erzbach) and 4 (Emsbach), because the downstream concentration increases correspond to the particularly enriched TMM of both tributaries. Both creeks are characterized by catchments with historic mines and mining heaps. This enables TMM inputs by leaching processes (Ciszewski et al., 2012) and the inflow of mine water, which can severely impact the chemistry of surface water (Jones et al., 2013;

Zhao and Marriott, 2013). In this context, the lower Lahn differs significantly from upstream areas where no significant TMM inputs from tributaries could be detected (Martin, 2019). That the high dissolved TMM concentrations of the tributaries 1 and 4 were focused on Mn, Co, Ni, Zn, and Cd is favored by the comparatively smaller retention of these elements in catchment soils and sediments (Tack et al., 1996; Hahn et al., 2018), as well as the weaker binding to Fe precipitates compared to elements such as Cu and Pb (Schaider et al., 2014). The TMM input of the tributary 4 into the Lahn is probably still underestimated in this study since the sampling point was located above an important mine water inflow (Supplementary material, Fig. S5) and the discharge quantities are estimated by the authors to be much higher than at tributary 1.

The similarity of dissolved P, V, As, and U as demonstrated in the PCA, is based on the relatively low variability of these elements in the Lahn River system, indicated by the mostly low EF (SPM) and CV (dissolved phase). The high percentages of the residual (F4) fraction underline a mostly lithogenic origin. Tributaries with over-average dissolved
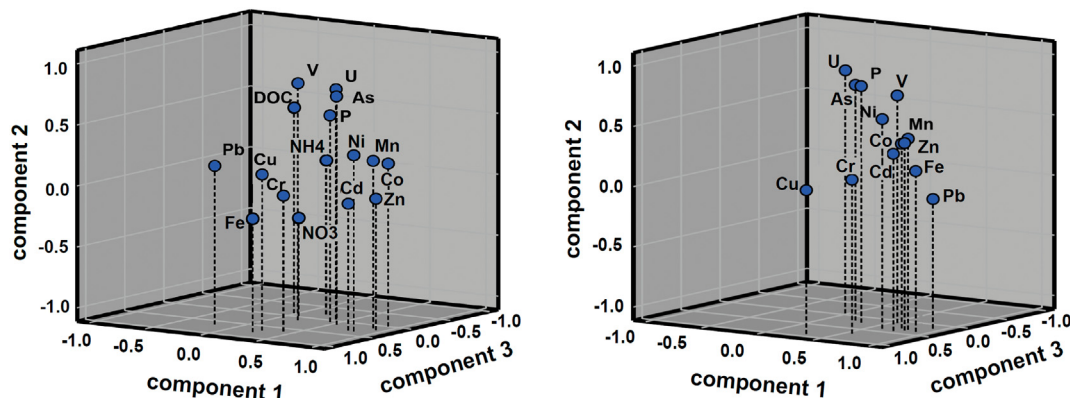

Fig. 5. A: Component plot of the dissolved concentrations of TMM, P, N-compounds, and DOC in rotated space. B: Component plot of the total TMM and P concentrations in rotated space.

concentrations of these elements have a rather negligible effect on the Lahn. Similar dynamics are explainable by the abundance of oxygen and the neutral to slightly alkaline conditions of the waters, which favors the formation of anionic compounds of As, P, and V in the form of arsenates, phosphates, and vanadates. Due to their similar molecular structure, these compounds are characterized by a similar solubility and can compete for sorption sites, while the reduction of positively charged surfaces under neutral to alkaline pH conditions reduces their binding possibilities (Shiller and Mao, 2000; Tu and Ma, 2003; Cheng et al., 2009; Dodds and Whiles, 2010; Rubinos et al., 2011). Uranium, which in oxygen-rich waters is usually present predominantly as UO_2^{2+}, is able to form anionic complexes, while the speciation of U may be closely linked to the formation of phosphates or vanadates (Cumberland et al., 2016).

Although Cu and Pb were more substantially enriched in SPM, similarities with Cr and Fe, as demonstrated by component 3 of the PCA, are expressed in low exchangeable (F1) concentrations. The generally high retention of Cr, Fe, Cu, and Pb is in accordance with investigations by Marqués et al. (2001), who found a comparatively higher release of Zn and Cd into running waters of a historical Pb/Zn mining region. In the case of the tributaries the CV of dissolved Cu and Pb were clearly lower than for Co, Mn, Ni, Zn, and Cd. Lenz (1986) reported enrichments of Cu and Pb in sediments of the tributaries 4 (Cu: 8–338 mg kg^{-1}; Pb: 74–1688 mg kg^{-1}) and 8 (Cu: 10–608 mg kg^{-1}; 89–306 mg kg^{-1}). Own investigations showed increased concentrations of Cu (258–282 mg kg^{-1}) and Pb (477–1030 mg kg^{-1}) in SPM of tributary 1 (Supplementary material, Table S9). Therefore, the decreased release of Cu and Pb in the concerned tributaries to the dissolved phase is only explainable by a stronger adsorption to soils, sediments, and SPM (Hahn et al., 2019).

With respect to nitrogen, the SPM samples show relatively small standard deviations. Compared to global rivers (Meybeck, 1982), the N_t concentrations and C/N ratios appear average. Also the variations of dissolved N-compounds, which do not show any significant concentration changes in the longitudinal course of the Lahn, can be regarded as rather balanced. Since N- and P-compounds typically enter surface waters together from municipal wastewater (Weigelhofer et al., 2018), the slightly increased NH$_4$ and P concentrations of the tributaries 7, 9, and 10 can be attributed to the influence of wastewater treatment plants located upstream. However, the slightly increased N and P concentrations of these tributaries are not enough to have a significant influence on the Lahn. Since during the wet season larger amounts of NO$_3$ tend to be discharged from the catchment areas into the rivers (Weber et al., 2020) and during the vegetation period it is increasingly integrated into the biomass of aquatic organisms (Chen et al., 2010), it is likely that the dissolved N concentrations of the Lahn are higher on an annual average than during the study period.

The results of the PCA reveal different variabilities in the concentrations of NH$_4$ and NO$_3$. This coincides with investigations by von der Wiesche and Wetzel (1998), who found different dynamics of NH$_4$ and NO$_3$ to be connected with different degradation and conversion rates. The various dynamics of TMM and N-compounds can be explained by diverse sources and different impacts by biogeochemical metabolic processes and instream biology (Xia et al., 2018).

4.3. Water phase (total concentrations)

The total contents of the water phase are closely related to the quantity and quality of SPM (Yang et al., 2014). Accordingly, the analysis of total contents without quantification of SPM concentrations, as practiced in this study, potentially increases the variability of total concentrations. Compared to the total concentrations determined by filtration, this method is associated with a correspondingly greater inaccuracy, but summarizes the variability of the total contents based on quantity and quality of the SPM in an element-specific manner. The decrease in the dissolved portions on the total concentrations of the Lahn

followed the order U > As, V, Ni, Zn > Cu, P > Mn, Co > Cd, Cr > Fe, Pb. This is almost identical to the proportions of dissolved and particulate TMM found in areas of the Elbe River (Germany) during a low water situation in 2003 by Baborowski et al. (2011). The low dissolved percentage on the total concentrations of Cr and Fe can be explained by the predominant binding of both elements in the crystal structure of mineral particles, which is indicated by high proportions in the residual (F4) fraction. The finding of high particulate contents of Cr and Fe is consistent with investigations by Pontér et al. (1990) and Pettine et al. (1992), who found 70–80% Fe (Kalix River, Sweden) and 40–97% Cr (Po River, Italy) in the particulate phase of other European rivers.

The relatively high particulate proportions of Mn, Co, Cd, and Pb are consistent with results of the sequential extraction of SPM, where the reducible (F2) fraction decreased in the order Pb > > Co > Cd > Mn > > other TMM. A comparatively high tendency of these TMM to be transported by (hydr-)oxide particles, but also by clay minerals, can therefore be assumed and is favored by the neutral to weakly alkaline pH conditions (Yang et al., 2014). However, it should be noted that the ratio of dissolved to total TMM may vary due to seasonal changes of pH and SPM content of the water phase (Resongles et al., 2015; Wen et al., 2013). The fact that especially the total concentrations of Fe, Mn, Co, Cd, and Pb simultaneously increased at the "OH" site, can be attributed to higher loads of SPM, especially since the dissolved TMM contents show no concentration peaks at this sampling location. Since the PCA grouped TMM preferentially bound to the reducible (F2) fraction (i.e. Mn, Fe, Co, Zn, Cd and Pb), TMM with higher dissolved concentrations (i.e. P, V, Ni, As, U) and TMM with binding preferences to the oxidizable (F3) and residual (F4) fraction (i.e. Cr, Cu), it can be assumed that the total concentrations of these groups are influenced differently under variable SPM concentrations of the water phase.

5. Conclusions

The investigations show that point sources of significant importance for a water system can be identified by the methodology applied. In areas of the Lahn River, this concerns in particular the dissolved concentrations of Mn, Co, Ni, Zn, and Cd. Due to their high mobility, these elements have a comparatively high potential to be released to the dissolved phase of surface waters, if a catchment shows similar conditions. For Pb, which was also enriched within SPM, a significantly lower release potential is demonstrated due to a higher binding affinity under the prevailing pH conditions. Using the Lahn as an example, it could be shown that relatively small tributaries can significantly influence the water quality of much larger watercourses during low water. This influence can differ substantially between the dissolved components and the solid phase. In this context, the release of TMM from mine water can play a particularly important role, since the discharge of mine water usually is less affected by periods of drought than its receiving water. Since running waters are frequently impacted by mine water, these effects can be assumed for many similar localities worldwide during low discharge periods.

While at least similar dynamics could partially be identified for P, V, As, and U, as well as for Cr, Fe, Cu, and Pb, the less clear traceability of their sources is based on relatively low enrichments and the absence of single dominant point sources within the study area, or on a high affinity for transport in the particulate phase (i.e. Pb). The fact that nitrogen compounds showed no similarities with TMM can be explained by the release from partially different sources and the stronger involvement in biological metabolic cycles.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.143110.

References

Alloway, B., 1999. Schwermetalle in Böden. Analytik, Konzentrationen, Wechselwirkungen. Spektrum, Berlin (Germany).

Baborowski, M., Büttner, O., Einax, J.W., 2011. Assessment of water quality in the Elbe River at low water conditions based on factor analysis. Clean – Soil, Air, Water 39 (5), 437–443. https://doi.org/10.1002/clen.201000373.

Bode, F. (Ed.), 1983. Die Mineralien und der Bergbau von Bad Ems. Emser Hefte. vol. 5. Rainer Bode Verlag, Bochum, p. 2 (Germany).

Cánovas, C.R., Riera, J., Carrero, S., Olías, M., 2018. Dissolved and particulate metal fluxes in an AMD-affected stream under different hydrological conditions: the Odiel River (SW Spain). Catena 165, 414–424. https://doi.org/10.1016/j.catena.2018.02.020.

Chen, D., Lu, J., Wang, H., Shen, Y., Kimberley, M.O., 2010. Seasonal variations of nitrogen and phosphorus retention in an agricultural drainage river in East China. Environ. Sci. Pollut. Res. 17, 312–320. https://doi.org/10.1007/s11356-009-0246-x.

Cheng, H., Hu, Y., Luo, J., Xu, B., Zhao, J., 2009. Geochemical processes controlling fate and transport of arsenic in acid mine drainage (AMD) and natural systems. J. Hazard. Mater. 165, 13–26. https://doi.org/10.1016/j.jhazmat.2008.10.070.

Ciszewski, D., Kubisk, U., Aleksander-Kwaterczak, U., 2012. Long-term dispersal of heavy metals in a catchment affected by historic lead and zinc mining. J. Soils Sediments 12, 1445–1462. https://doi.org/10.1007/s11368-012-0558-1.

Cumberland, S.A., Douglas, G., Grice, G., Moreau, J.W., 2016. Uranium mobility in organic-rich sediments: a review of geological and geochemical processes. Earth Sci. Rev. 159, 160–185. https://doi.org/10.1016/j.earscirev.2016.05.010.

Delpla, I., Jung, A.V., Baures, E., Clement, M., Thomas, O., 2009. Impacts of climate change on surface water quality in relation to drinking water production. Environ. Int. 35, 1225–1233. https://doi.org/10.1016/j.envint.2009.07.001.

DLR (Dienstleistungszentrum Ländlicher Raum Rheinland-Pfalz), 2019. Vieljähriges Mittel (1961–1990) der Wetterstation Koblenz-Horchheim. http://www.am.rlp.de/Internet/AM/NotesAM.nsf/amweb/95563ad919208bbfc1257171002e8a6b?OpenDocument&TableRow=2.1.1.%2C2.7#2.1. (accessed 4th December 2019).

Dodds, W.K., Whiles, M.R., 2010. Freshwater Ecology. Concepts and Environmental Applications of Limnology. 2nd edn. Elsevier, Amsterdam (Netherlands) https://doi.org/10.1016/B978-0-12-374724-2.00014-3.

Dragun, Z., Kapetanović, D., Raspor, B., Teskeredžić, E., 2011. Water quality of medium size watercourse under baseflow conditions: the case study of river Sutla in Croatia. AMBIO 40, 391–407. https://doi.org/10.1007/s13280-010-0119-z.

Dung, T.T.T., Cappuyns, V., Swennen, R., Phung, N.K., 2013. From geochemical background determination to pollution assessment of heavy metals in sediments and soils. Rev. Environ. Sci. Biotechnol. 12, 335–353. https://doi.org/10.1007/s11157-013-9315-1.

EEA (European Environment Agency), 2010. The European Environment. State and Outlook 2010 – Freshwater Quality. Publications Office of the European Union, Luxembourg. https://www.eea.europa.eu/soer/europe/freshwater-quality (accessed 12th December 2019).

Elbaz-Poulichet, F., Seidel, J.L., Casiot, C., Tusseau-Vuillemin, M.H., 2005. Short-term variability of dissolved trace element concentrations in the Marne and seine Rivers near Paris. Sci. Total Environ. 367, 278–287. https://doi.org/10.1016/j.scitotenv.2005.11.009.

Foulds, S.A., Brewer, P.A., Macklin, M.G., Haresign, W., Betson, R.E., Rassner, S.M.E., 2014. Flood-related contamination in catchments affected by historical metal mining: an unexpected and emerging hazard of climate change. Sci. Total Environ. 476 (477), 165–180. https://doi.org/10.1016/j.scitotenv.2013.12.079.

Froger, C., Ayrault, S., Evrard, O., Monvoisin, G., Bordier, L., Lefèvre, I., Quantin, C., 2018. Tracing the sources of suspended sediment and particle-bound trace metal elements in an urban catchment coupling elemental and isotopic geochemistry, and fallout radionuclides. Environ. Sci. Pollut. Res. 25, 28667–28681. https://doi.org/10.1007/s11356-018-2892-3.

Gaillardet, J., Viers, J., Dupré, B., 2003. Trace elements in river waters. In: Drever, J.I. (Ed.), Treatise on Geochemistry. Surface and Groundwater, Weathering and Soils. Elsevier, Amsterdam (Netherlands), pp. 225–272 https://doi.org/10.1016/B0-08-043751-6/05165-3.

Garbarino, J.R., Hoffman, G.L., 1999. Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory, Comparison of a Nitric Acid in-Bottle Digestion Procedure to Other Whole-Water Digestion Procedures. Open File Rep. 99–094. U.S. Geological Survey, Denver, Colorado (USA).

Gozzard, E., Mayes, W.M., Potter, H.A.B., Jarvis, A.P., 2011. Seasonal and spatial variation of diffuse (non-point) source zinc pollution in a historically metal mined river catchment, UK. Environ. Pollut. 159, 3113–3122. https://doi.org/10.1016/j.envpol.2011.02.010.

Hahn, J., Opp, C., Zitzer, N., Laufenberg, G., 2016. Impacts of river impoundment on dissolved trace metals in floodplain soils of the Lahn River (Germany). Environ. Earth Sci. 75, 1141. https://doi.org/10.1007/s12665-016-5950-5.

Hahn, J., Zitzer, N., Laufenberg, G., 2018. The effect of catchment soils on heavy metal concentrations in a brook situated in the historic mining region of Braubach. Germany. Die Erde 149 (2–3), 132–144. https://doi.org/10.12854/erde-2018-401.

Hahn, J., Opp, C., Ganzenmüller, R., Ewert, A., Schneider, B., Zitzer, N., Laufenberg, G., 2019. Catchment soils as a factor of trace metal accumulation in sediments of the reservoir Klingenberg (eastern Ore Mountains, Germany). J. Environ. Sci. 86, 1–14. https://doi.org/10.1016/j.jes.2019.05.002.

Hauenstein, M., Hutzler-Gardt, U., 1996. Inventur der Gehalte an Spurenelementen und organischen Schadstoffen in Böden von Rheinland-Pfalz. In: Forsten, Ministerium für Umwelt und (Ed.), Bodenbelastungskataster Rheinland Pfalz, Mainz, Germany, pp. 1–212.

Helios Rybicka, E., Adamiec, E., Aleksander-Kwaterczak, U., 2005. Distribution of trace metals in the Odra River system: water–suspended matter–sediments. Limnologica 35, 185–198. https://doi.org/10.1016/j.limno.2005.04.002.

IPCC, 2014. In: Team, Core Writing, Pachauri, R.K., Meyer, L.A. (Eds.), Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. IPCC, Geneva, Switzerland (151 pp).

Javed, M.B., Shotyk, W., 2018. Estimating bioaccessibility of trace elements in particles suspended in the Athabasca River using sequential extraction. Environ. Pollut. 240, 466–474. https://doi.org/10.1016/j.envpol.2018.04.131.

Jochum, J., 2000. Variscan and post-Variscan lead-zinc mineralization, Rhenish massif, Germany: evidence for sulfide precipitation via thermochemical sulfate reduction. Mineral. Deposita 35 (5), 451–464. https://doi.org/10.1007/s001260050255.

Jones, A., Rogerson, M., Greenway, G., Potter, H.A.B., Mayes, W.M., 2013. Mine water geochemistry and metal flux in a major historic Pb-Zn-F orefield, the Yorkshire Pennines, UK. Environ. Sci. Pollut. Res. 20, 7570–7581. https://doi.org/10.1007/s11356-013-1513-4.

Keβler, S., Pohlert, T., Breitung, V., Wilcsek, K., Bierl, R., 2020. Comparative evaluation of four suspended particulate matter (SPM) sampling devices and their use for monitoring SPM quality. Environ. Sci. Pollut. Res. 27, 5993–6008. https://doi.org/10.1007/s11356-019-07314-0.

Lenz, W., 1986. Untersuchungen zur Schwermetallbelastung und –mobilität im ehemaligen Blei/Zink Revier Bad Ems/Holzappel. Gießener Geologische Schriften, Gießen (Germany), p. 40.

Liu, C., Fan, C., Shen, Q., Shao, S., Zhang, L., Zhou, Q., 2016. Effects of riverine suspended particulate matter on post-dredging metal re-contamination across the sediment-water interface. Chemosphere 144, 2329–2335. https://doi.org/10.1016/j.chemosphere.2015.11.010.

LVermGeoRP (Landesamt für Vermessung und Geobasisinformation Rheinland-Pfalz), 2020. Topographische Karte 1:25000, Kartenblatt 5711, Koblenz (Germany).

Marqués, M.J., Matrínez-Conde, E., Rovira, J.V., Ordóñez, S., 2001. Heavy metals pollution of aquatic ecosystems in the vicinity of a recently closed underground lead-zinc mine (Basque Country, Spain). Environ. Geol. 40 (9), 1125–1137. https://doi.org/10.1007/s002540100314.

Martin, C.W., 2019. Trace metal concentrations along tributary streams of historically mined areas, lower Lahn and Dill River basins, Central Germany. Catena 174, 174–183. https://doi.org/10.1016/j.catena.2018.11.008.

Masson, M., Angot, H., Le Bescond, C., Launay, M., Dabrin, A., Miègel, C., Le Coz, J., Coquery, M., 2018. Sampling of suspended particulate matter using particle traps in the Rhône River: relevance and representativeness for the monitoring of contaminants. Sci. Total Environ. 637–638, 538–549. https://doi.org/10.1016/j.scitotenv.2018.04.343.

Mc Cleskey, R.B., Nordstrom, K.D., Ryan, J.N., 2012. Electrical conductivity method for natural waters. Appl. Geochem. 26, 227–229. https://doi.org/10.1016/j.apgeochem.2011.03.110.

Meybeck, M., 1982. Carbon, nitrogen, and phosphorus transport by world rivers. Am. J. Sci. 282, 401–450. https://doi.org/10.2475/ajs.282.4.401.

Mohaupt, V., Sieber, U., van den Roovaart, J., Verstappen, C.G., Langenfeld, F., Braun, M., 2001. Diffuse sources of heavy metals in the Rhine basin. Water Sci. Technol. 44 (7), 41–49. https://doi.org/10.2166/wst.2001.0385.

Moraetis, D., Stamati, F., Kotronakis, M., Fragia, T., Paranychnianakis, N., Nikolaidis, N.P., 2011. Identification of hydrologic and geochemical pathways using high frequency sampling, REE aqueous sampling and soil characterization at Koiliaris critical zone observatory. Crete. Appl. Geochem. 26, 101–S104. https://doi.org/10.1016/j.apgeochem.2011.03.055.

Mueller, G., 1986. Schadstoffe in Sedimenten – Sedimente als Schadstoffe. Mitteilungen der Österreichischen Geologischen Gesellschaft 79, 107–126.

Nordstrom, K.D., 2009. Acid rock drainage and climate change. J. Geochem. Expl. 100, 97–104. https://doi.org/10.1016/j.gexplo.2008.08.002.

Ödman, F., Ruth, T., Pontér, C., 1999. Validation of a field filtration technique for characterization of suspended particulate matter from freshwater. Part I. Major elements. Appl. Geochem. 14, 301–317. https://doi.org/10.1016/S0883-2927(98)00050-X.

Ödman, F., Ruth, T., Pontér, C., 2006. Validation of a field filtration technique for characterization of suspended particulate matter from freshwater. Part II. Minor, trace and ultra trace elements. Appl. Geochem. 21 (12), 2112–2134. https://doi.org/10.1016/j.apgeochem.2006.06.010.

OGewV, 2016. Verordnung zum Schutz von Oberflächengewässern (Oberflächengewässerverordnung - OgewV). Bundesgesetzblatt Jahrgang 2016, Teil I Nr. 28, (23.06.2016). p. 1373 (Bonn (Germany).

Olías, M., Nieto, J.M., Sarmiento, A.M., Ceron, J.C., Cánovas, C.R., 2004. Seasonal water quality variations in a river affected by acid mine drainage: the Odiel River (south West Spain). Sci. Total Environ. 333, 267–281.

Pettine, M., Camusso, M., Martinotti, W., 1992. Dissolved and particulate transport of arsenic and chromium in the Po River (Italy). Sci. Total Environ. 119, 253–280. https://doi.org/10.1016/0048-9697(92)90268-W.

Pontér, C., Ingri, J., Burman, J.O., Boström, J., 1990. Temporal variations in dissolved and suspended iron and manganese in the Kalix River, northern Sweden. Chem. Geol. 81, 121–131. https://doi.org/10.1016/0009-2541(90)90042-6.

Rauret, G., Lopez-Sanches, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., Quevauviller, P., 1999. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. J. Environ. Monitor. 1 (1), 57–61. https://doi.org/10.1039/A807854H.

Resongles, E., Casiot, C., Freydier, R., Le Gall, M., Elbaz-Poulichet, F., 2015. Variation of dissolved and particulate metal(loid) (as, cd, Pb, Sb, Tl, Zn) concentrations under varying discharge during a Mediterranean flood in a former mining watershed, the Gardon River (France). J. Geochem. Explor. 158, 132–142. https://doi.org/10.1016/j.gexplo.2015.07.010.

Rinklebe, J., Antoniadis, V., Shaheen, S.M., Rosche, O., Altermann, M., 2019. Health risk assessment of potentially toxic elements in soils along the central Elbe River, Germany. Environ. Int. 126, 76–88. https://doi.org/10.1016/j.envint.2019.02.011.

Romero, E., Le Gendre, R., Garnier, J., Billen, G., Fisson, C., Silvestre, M., Riou, P., 2016. Long-term water quality in the lower seine: lessons learned over 4 decades of monitoring. Environ. Sci. Pol. 58, 141–154. https://doi.org/10.1016/j.envsci.2016.01.016.

Rubinos, D.A., Iglesias, L., Díaz-Fierros, F., Barral, M.T., 2011. Interacting effect of pH, phosphate and time on the release of arsenic from polluted river sediments (Anllóns River, Spain). Aquat. Geochem. 17, 281–306. https://doi.org/10.1007/s10498-011-9135-2.

Runkel, R.L., Kimball, B.A., Nimick, D.A., Walton-Day, K., 2016. Effects of flow regime on metal concentrations and the attainment of water quality standards in a remediated stream reach, Butte, Montana. Environ. Sci. Technol. 50, 12641–12649. https://doi.org/10.1021/acs.est.6b03190.

Salminen, R., 2005. Geochemical Atlas of Europe, Part 1, Background Information, Methodology and Maps. Geological Survey of Finland, Espoo http://weppi.gtk.fi/publ/foregsatlas/index.php (accessed 30th September 2020).

Schaider, L.A., Senn, D.B., Estes, E.R., Brabander, D.J., Shine, J.P., 2014. Sources and fates of heavy metals in a mining-impacted stream: temporal variability and the role of iron oxides. Sci. Total Environ. 490, 456–466. https://doi.org/10.1016/j.scitotenv.2014.04.126.

Scheid, R., 1994. Der Holzappeler Gangzug mit "Grube Holzappel". Kreisverwaltung Rhein-Lahn. Bergbau im Rheinlan-Kreis, Bad Ems (Germany), pp. 46–49.

Schroeder, H., Fabricius, A.-L., Ecker, D., Ternes, T.A., Duester, L., 2017. Metal(loid) speciation and size fractionation in sediment pore water depth profiles examined with a new meso profiling system. Chemosphere 179, 185–193. https://doi.org/10.1016/j.chemosphere.2017.03.080.

Sedlmeier, K., Feldmann, H., Schädler, G., 2018. Compound summer temperature and precipitation extremes over Central Europe. Theor. Appl. Climatol. 131, 1493–1501. https://doi.org/10.1007/s00704-017-2061-5.

Seeliger, A., Buchert, D.E., Noll, T., 2009. Der Emser Gangzug. Der Aufschluss 60 (2/3), 66–99.

Shiller, A.M., Mao, L., 2000. Dissolved vanadium in rivers: effects of silicate weathering. Chem. Geol. 165, 13–22. https://doi.org/10.1016/S0009-2541(99)00160-6.

Tack, F.M., Callewaert, O.W.J.J., Verloo, M.G., 1996. Metal solubility as a function of pH in a contaminated, dredged sediment affected by oxidation. Environ. Pollut. 91 (2), 199–208. https://doi.org/10.1016/0269-7491(95)00049-6.

Tu, C., Ma, L.Q., 2003. Effects of arsenate and phosphate on their accumulation by an arsenic-hyperaccumulator *Pteris vittata* L. Plant Soil 249, 373–382. https://doi.org/10.1023/A:1022837217092.

Weber, G., Honecker, U., Kubiniok, J., 2020. Nitrate dynamics in springs and headwater streams with agricultural catchments in southwestern Germany. Sci. Total Environ. 722, 137858. https://doi.org/10.1016/j.scitotenv.2020.137858.

Weigelhofer, G., Hein, T., Bondar-Kunte, E., 2018. Phosphorus and nitrogen dynamics in riverine systems. Human impacts and management options. In: Schmutz, S., Sendzimir, J. (Eds.), Riverine Ecosystem Management. Springer, Amsterdam (Netherlands), pp. 187–202.

Wen, Y., Yang, Z., Xia, X., 2013. Dissolved and particulate zinc and nickel in the Yangtze River (China): distribution, sources and fluxes. Appl. Geochem. 31, 199–208. https://doi.org/10.1016/j.apgeochem.2013.01.004.

Wieber, G., 1994. Das ehemalige Erzrevier an der Unteren Lahn. Hydro- und geochemische sowie umweltgeologische Verhältnisse unter Berücksichtigung der Rückstände aus der Erzaufbereitung. Gießener Geologische Schriften, Gießen, p. 52 (Germany).

von der Wiesche, M., Wetzel, A., 1998. Temporal and spatial dynamics of nitrite accumulation in the Lahn River. Wat. Res. 32 (5), 1653–1661. https://doi.org/10.1016/S0043-1354(97)00376-X.

Xia, X., Zhang, S., Li, S., Zhang, L., Wang, G., Zhang, L., Wang, J., Li, Z., 2018. The cycle of nitrogen in river systems: sources, transformation, and flux. Environ Sci Process Impacts 20, 863–891. https://doi.org/10.1039/c8em00042e.

Xiao, J., Wang, L., Deng, L., Jin, Z., 2019. Characteristics, sources, water quality and health risk assessment of trace elements in river water and well water in the Chinese loess plateau. Sci. Total Environ. 650, 2004–2012. https://doi.org/10.1016/j.scitotenv.2018.09.322.

Yang, Z., Xia, X., Wang, Y., Ji, J., Wang, D., Hou, Q., Yu, T., 2014. Dissolved and particulate partitioning of trace elements and their spatial–temporal distribution in the Changjiang River. J. Geochem. Explor. 145, 114–123. https://doi.org/10.1016/j.gexplo.2014.05.013.

Zerling, L., Hanisch, C., Junge, F.W., 2006. Heavy metal inflow into the floodplains at the mouth of the river Weiße Elster (Central Germany). Acta Hydrochim. Hydrobiol. 34, 234–244. https://doi.org/10.1002/aheh.200400624.

Zhao, Y., Marriott, S.B., 2013. Dispersion and remobilisation of heavy metals in the river Severn system, UK. Procedia Environ. Sci. 18, 167–173. https://doi.org/10.1016/j.proenv.2013.04.022.