The effect of catchment soils on heavy metal concentrations in a brook situated in the historic mining region of Braubach, Germany

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Abstract

Forest soils located in the region of Braubach (Rhineland-Palatinate, Germany) are characterized by elevated concentrations of cadmium (Cd), copper (Cu), and lead (Pb), resulting from local heavy metal emissions. The regional geomorphology is dominated by the low mountain range of the Rheinish Massif and the frequent occurrence of V-shaped valleys crossed by small tributaries of the Rhine River. The frequent occurrence of steep valley slopes should theoretically facilitate the influence of polluted forest soils on brooks of the valley bottoms by intensified processes of slope water influx and soil erosion. To investigate pollution state and soil-water interactions in a heavy metal enriched catchment, concentrations of Cd, Cu, and Pb were determined for catchment soils, sediment, suspended matter, and surface water of a brook situated close to a former smelter area. Heavy metal binding was characterized by BCR sequential extraction method. Total concentrations of Cd increased with the transition from catchment soils to brook sediments and suspended matter, while the proportions of the analyzed binding fractions partially changed. The concentrations of Cu and Pb in soils were marked by a higher heterogeneity and exceeded the concentrations found in sediments and suspended matter. For Pb, the proportions of binding fractions were relatively static, whereas the Cu binding fractions in suspended matter clearly differed in comparison with soils and sediments. For all studied heavy metals, an increase in the concentration of the respective dissolved fraction was found along the course of the brook.

Zusammenfassung

Waldböden in der Umgebung von Braubach (Rheinland-Pfalz) sind geprägt von erhöhten Konzentrationen an Cadmium (Cd), Kupfer (Cu) und Blei (Pb) als Langzeitfolge regionaler Schwermetallfreisetzung. Die geomorphologischen Merkmale der Region sind bedingt durch den Gebirgsrumpf des Rheinishen Schiefergebirges, der von den Kerbtälern kleiner Nebengewässer des Rhins durchschnitten wird. Das relativ steile Gefälle der Talhänge sollte theoretisch, über Hangwasserzufluss und Erosionsprozesse, die von belasteten Waldböden der Unterhangbereiche erfolgenden Stoffausträge in die Gewässer der Talböden begünstigen. Um den Belastungsstatus und die Interaktionen von Böden und Fließgewässern in einem mit Schwermetallen angereichertem Einzugsgebiet zu untersuchen, wurden die Konzentrationen von Cd, Cu und Pb in Böden des Einzugsgebietes, Sedimenten, Schwebstoffen und Wässern eines Baches analysiert, der unweit eines ehemaligen Verhüttungsbetriebes gele-

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structive impact of heavy metal emissions during ore processing and smelting (Rieuwerts and Far ago 1995: 113ff.; Ullricha et al. 1999: 190ff.; Musilova et al. 2016: 570). A primary heavy metal release can occur when mined ores are crushed, separated and the waste material is disposed to spoil heaps. The de-
occur when mined ores are crushed, separated and the waste material is disposed to spoil heaps. The de-
position heavy metal-bearing particles can be eroded and transferred to adjacent soils or watercourses (Schmidt et al. 1998: 17). A leaching of mining waste by surface (Cánovas et al. 2012) or groundwater (Aleksander-Kwaterzak and Helios-Rybicka 2009: 20) can induce an additional output of metallic compounds. A further release takes place during the smelting process when heavy metals partly separate from the heated ores and are emitted as aerosols (Csavina et al. 2011: 145ff.). In the atmosphere, heavy metals can be transported across long distances (Hong et al. 1994: 1841ff.) before they precipitate as dry or wet de-
position (Berkvist et al. 1989: 260). After deposition, heavy metals are bound to organic or inorganic particles of sediments or soils and can be accumulated in dependence on input quantity and sorption capacity. To what extent a heavy metal is bound to the com-
ponents of sediments or soils is determined by numerous factors such as the element total concentration (Hornburg and Brümmer 1993: 476), pH- and redox conditions (Gambrell et al. 1991: 364), or the specific mobility behavior of each element (Herms and Brüm-
mer 1984: 403ff.). Heavy metal-enriched sediments or soils may act as pollutants when these elements are transferred to pore or surface water through desorption processes (Salomons et al. 1987: 18ff.). Hence, the chemical characteristics of catchment soils, sedi-
ments, and surface water in mining areas are strongly determined by anthropogenic impacts and mutual

1. Introduction

Above-average heavy metal concentrations in soils and water typically occur in mining regions as the consequential impact of heavy metal emissions during ore processing and smelting (Rieuwerts and Fara go 1995: 113ff.; Ullricha et al. 1999: 190ff.; Musilova et al. 2016: 570). A primary heavy metal release can occur when mined ores are crushed, separated and the waste material is disposed to spoil heaps. The de-
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mer 1984: 403ff.). Heavy metal-enriched sediments or soils may act as pollutants when these elements are transferred to pore or surface water through desorption processes (Salomons et al. 1987: 18ff.). Hence, the chemical characteristics of catchment soils, sedi-
ments, and surface water in mining areas are strongly determined by anthropogenic impacts and mutual interactions of these environmental compartments (Vega et al. 2004: 143ff.; Zhang et al. 2012: 2262ff.). Especially forest soils are strongly influenced by atmos-
pheric metal deposition, which is due to the precipi-
tation of metal bearing aerosol droplets at the surfaces of leaves or needles (Mayer 1983: 47). In ad-
dition, steep-sloped forests typically act as headwa-
ter for brooks (Sidle et al. 2000: 370). These facts en-
force the suggestion that atmospherically deposited heavy metals are partly transferred from catchment soils to headwaters when the retention capability of a soil is exceeded. The heavy metal release from soil to pore water varies with element mobility and the pollution state and properties of a soil (Du Laing et al. 2009: 2924ff.; Hahn et al. 2016: 7ff.). In streams, however, the load and binding fractions of an element can clearly differ between sediments and suspended matter (Adamiec and Helios-Rybicka 2002: 678; Helios-
Rybicka et al. 2005: 196). This raises the question to which extent heavy metal accumulations in forest soils affect the quality of sediments and suspended matter of local brooks and if this process is influenced by element-specific mobility behavior. To exemplarily study the transfer paths of cadmium (Cd), copper (Cu), and lead (Pb) between a small scale catchment and running water, investigations were carried out on for-
ested catchment soils, sediments, and suspended matter of a brook situated in the historic mining region of Braubach (Germany).

2. Study sites

The study area is located in the Rhenish Massif at the borderland between the Taunus mountain range and the Middle Rhine Valley. Annual precipitation of the surrounding region is 675 mm, the average tempera-
ture is 10.4 °C (DLR 2017), the main wind direction is southwest (van Saan 1995: 14). The geology is domi-
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nated by the small-scale differentiated occurrence of Devonian shale, quartzite, greywacke, and siltstone, which were folded during the Variscan orogeny (Walter 2007: 194). During Paleocene and Tertiary phases of tectonic activity, hydrothermal water locally rose along tectonic disturbances, leading to the hydrothermal formation of chemically varying ore deposits (Seelig er et al. 2009: 76ff.). After the partial erosion of this mountain range during late Paleozoic and Mesozoic times (Sauer and Felix-Henningsen 2006: 7ff.), the development of the current landscape was strongly influenced by a Quarternary uplift of the leveled rock mass (Demoulin and Hallot 2009: 696ff.). This relatively quick uplift facilitated the downcutting erosion of the Rhine River and the development of steep valleys of its tributaries during late Quarternary (Meyer and Stets 2002: 2018). Therefore, the region’s present topography is characterized by plateau areas with relatively low gradients, reaching altitudes of around 250 to 350 meters. These plateau areas are divided by relatively steep valleys, generated by small brooks which join the Rhine River at an elevation of around 70 meters. The earliest metallurgic activities in Braubach were conducted during the early Latène era by the Celtic population (Joachim 1991: 6) and were continued with varying intensity during the Middle Ages and the Early Modern Period (David 2001: 11). A progression of mainly Cu-, Pb-, and Zn-mining started in the second half of the 19th century. In parallel, the local smelter developed to the probably largest producer of Pb in Germany during the 1930s, reaching a production of 40,000 tons in 1939 (David 1991: 45). After the last mine was closed in 1963, the smelter complex was run as secondary smelter before it was transformed into a recycling company. Since the late 19th century the generated fume was channelized and led from the smelter area to three elevated vents situated within the adjacent forest (Lambert 2011: 44). Consequences of the heavy metal release during ore procession were accumulations of Cd and Pb in forest soils (van Saan 1995: 33ff.), earthworms (Emmerling et al. 1997: 34ff.), isopods (Dallinger and Prosi 1988: 100) or diplopods (Köhler et al. 1995: 39ff.).

The investigations were conducted in a valley which was regarded to be representative of morphology, vegetation, and hydrology for the forested areas around Braubach. The observed brook is fed by several sources situated 270-280 m above sea level, close to the low mountain plateau area. The watercourse is interrupted by a small street and a historic dumping ground, dividing it into an upper and a lower valley section. The brook joins the Mühlbach Brook, a small tributary of the Rhine River, after a length of 1.5 kilometers and the passage of 170-180 meters in altitude. The study area is located northeastern to the historic smelter’s vents (Fig. 1). As the most common prevailing wind direction is southwest, the sampling area is located within the potential main direction of atmospheric heavy metal deposition (van Saan 1995: 14). Soils situated within the lower valley section may increasingly be influenced by the historic smelting area and a removed smelting heap.

![Fig. 1 Overview of the study area in Germany and potential sources of heavy metal pollution. Source: Own elaboration based on LWermGeoRP (2017)](image-url)
and five soils from the valley bottom. Soil samples were collected from increments of 0-10 cm and 20-30 cm depth. Brook sediments were sampled at eleven sites along the valley (Fig. 2) from a depth of 0-10 cm. Suspended matter and water were sampled during a period of six weeks (29 March to 14 May 2017) at two stationary sampling sites situated in the upper (S1) and the lower section (S2) of the studied brook.

3.2 Sample preparation

Soils and sediments were collected as disturbed samples. The suspended matter was collected in 500 ml beakers which were angularly attached inside the brook so that the opening was located between one centimeter below and one centimeter above the water table. The beakers were emptied weekly. Soil, sediment, and suspended matter were air-dried, homogenized in a porcelain mortar and sieved (< 2 mm) prior to analysis. Water samples were collected daily in polyethylene (PE) syringes from two centimeters below the water table. The fresh samples were divided into two halves. The first half remained untreated for the analysis of total organic carbon (TOC). The second half was filtered by 0.45 micron syringe filters (Minisart NML, Cellulose Acetate Membrane, Sartorius, Göttingen, Germany) to obtain the dissolved element fraction. The filtered sample was subsequently acidified at a water/HNO₃ ratio of 100:1. All water samples were stored in a refrigerator at -18 °C until analysis.

3.3 Field measurements

Soil sampling sites were documented in the angle of inclination by means of a clinometer. Soil types were defined according to IUSS Working Group WRB (2015). Geographical coordinates and altitudes of each sampling site were obtained by means of GPS. Electrical conductivity (EC), temperature (°C), and acidity (pH) of brook water were determined simultaneously to the daily collection of water samples with a portable multi-meter and adequate electrodes (Multiline P4, WTW, Weinheim, Germany). Discharge rates were estimated by collecting brook water during a defined time interval along stationary cross-sections. The water which was collected in plastic bags was weighed with portable scales. Each measurement was replicated six times. The average weight was equaled to the discharge amount.

3.4 Laboratory work

Air-dried samples of the soils, the sediments, and the suspended matter were used to determine pH, textures, and heavy metal contents. The pH value was measured by suspending the samples in 0.01 mol CaCl₂ which was added to each sample in a proportion of 1:2.5 (DIN 2005). After shaking the suspensions for two hours, the pH value was determined with a glass electrode. Textures were analyzed by a combined
sieve and pipette analysis after organic substances were oxidized by H₂O₂ and Na₄P₂O₇ was added to the suspensions (DIN 2002).

Heavy metal contents were analyzed by using the revised BCR sequential extraction procedure (Rauret et al. 1999: 58ff.). This sequential extraction method consists of four extraction steps (Table 1), which divide the heavy metal content in an exchangeable, a reducible, an oxidizable, and a residual fraction. Concentrations of Cd, Cu, and Pb in soil extracts were determined by Flame Atomic Absorption Spectrometry (Perkin Elmer AAnalyst 400, Perkin Elmer, Rodgau Jüngesheim, Germany). Concentrations of dissolved Cd, Cu, and Pb in water samples were measured by ICP-mass spectrometry (X-Series 2, Thermo Fisher, Dreieich, Germany).

TOC of water samples was measured by using a TOC analyzer (DimatOC 2000, Dimatoc, Essen, Germany). Organic carbon (Corg) in the soil, the sediment, and the suspended matter was determined in oven-dried (105°C) samples, which were ground in a pebble mill prior to analysis. Two replicates of each sample were heated at 950°C and detected in a C/N analyzer (vario EL cube, Elementar, Langenselbold, Germany). Corg was calculated as the average concentration of both replicates. A correlation analysis was conducted for all generated data using IBM SPSS Statistics 23. All data were controlled for a normal distribution by Kolmogorov-Smirnov-Test. The correlation analysis was conducted by using Spearman’s Rank correlation after a non-normal distribution was observed.

4. Results

4.1 Water characteristics

Brook water was characterized by a discharge ranging from 0.12 to 2.39 liters per second during the sampling period (29 March to 14 May 2017). At the beginning, the discharge rate was clearly higher than at the campaign’s end, likely resulting from increasing temperatures during the ongoing spring. As an effect of a steeper gradient of the valley bottom, at sampling site 1 a slightly higher discharge rate was found than at sampling site 2 (Table 2). The pH was slightly alka-

Table 1  Sequential extraction steps according to Rauret et al. (1999: 58ff.)

<table>
<thead>
<tr>
<th>Fraction and binding forms</th>
<th>Extraction procedure (1g sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1 exchangeable: mobile and easy to mobilize</td>
<td>shaking for 16h in 50 ml of 0.11 mol/l acetic acid (C₂H₄O₂)</td>
</tr>
<tr>
<td>F2 reducible: bound to Fe/Mn (hydr-)oxides</td>
<td>shaking for 16h in 40 ml of 0.5 mol/l hydroxyl-ammonium chloride ((NH₃OH)Cl)</td>
</tr>
<tr>
<td>F3 oxidizable: organically bound (in high stable metal-organic complexes)</td>
<td>digestion in 10 ml 8.8 mol/l hydrogen peroxide (H₂O₂), shaking for 16h in in 50 ml 1.0 mol/l ammonium acetate (C₂H₇NO₂)</td>
</tr>
<tr>
<td>F4 residual: bound in the crystalline structure of minerals</td>
<td>heating for 2h in aqua regia</td>
</tr>
</tbody>
</table>

Table 2  Mean values of temperature (°C), electrical conductivity, pH, TOC, discharge (l/sec), and dissolved concentrations of Cd, Cu, and Pb (n = number of samples). Source: Own elaboration

<table>
<thead>
<tr>
<th>Site</th>
<th>°C</th>
<th>EC</th>
<th>pH</th>
<th>TOC</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>l/sec</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µS/cm</td>
<td></td>
<td></td>
<td>(%)</td>
<td>(µg/l)</td>
<td>(µg/l)</td>
<td>(µg/l)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site 1</td>
<td>8.6</td>
<td>274</td>
<td>7.9</td>
<td>20.9</td>
<td>0.054</td>
<td>3.21</td>
<td>2.14</td>
<td>1.07</td>
<td>47</td>
</tr>
<tr>
<td>Site 2</td>
<td>9.5</td>
<td>369</td>
<td>8.2</td>
<td>25.6</td>
<td>0.17</td>
<td>8.09</td>
<td>6.48</td>
<td>0.79</td>
<td>47</td>
</tr>
</tbody>
</table>
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line and varied from pH 7.6 to 8.3 within the whole sample series. Electrical conductivity varied from 230 to 397 μS/cm, TOC reached values between 4.83% and 47.5%. At sampling site 2, both parameters reached comparatively higher values. A similar tendency was found for dissolved heavy metal concentrations, as dissolved Cu increased with an average factor of 2.3 and dissolved Cd and Pb increased with an average factor of 3 between both sampling sites.

4.2 Soil characteristics

Within the 15 investigated soil profiles, a total of six different soil types could be distinguished. Soils sampled in low slope positions with inclination angles of 24° to 45° were, with the exception of one semi-terrestrial soil, classified as terrestrial soils. The soil types varied in their spatial distribution mainly between Dystric Cambisols, Colluvic Cambisols, and Cambic Leptosols, whereby the sampled profiles also included one Colluvic Leptosol and one Haplic Gleysol. With regard to their distribution, the majority of Dystric Cambisols and the Haplic Gleysol were situated along slope positions of the upper valley section. In opposite, Cambic Leptosols, Colluvic Cambisols, and the Colluvic Leptosol were restricted to the valley's lower section. Independent from their position within the valley, soils situated on the valley bottom were consistently marked by the presence of fluvial sediments and groundwater influence. Therefore, these soils were uniformly classified as Gleyic Fluvisols (IUSS Working Group WRB 2015: 12ff.). Grain size distribution showed no clear trends in the comparison of the different soil groups (Table 3). Grain fractions were marked by relatively balanced amounts of sand, silt, and clay, mostly reaching maximal percentages in the sand fraction. All soil textures varied between sandy and clayey loam. Grain sizes of brook sediments were similar to the textures of catchment soils and were as well classified as sandy loams. The suspended matter was marked by a comparatively finer texture which is expressed in increasing silt contents. The sand fraction comprised, if present, almost exclusively fine sand. From sampling site 1 to sampling site 2, proportions of clay significantly increased. The highest concentrations of C\text{org} were measured in the Colluvic Leptosol and lowest in the Cambic Leptosols. All investigated soils were marked by decreasing concentrations of C\text{org} with the transition from 0-10 cm to 20-30 cm depth. Suspended matter of both sampling sites contained relatively high C\text{org} contents with relatively small concentration ranges. Soil pH-values showed distinct spatial differences. Dystric Cambisols and Colluvic Cambisols were marked by strong acidic conditions. Slightly acidic to neutral conditions were observed for the Gleyic Fluvisols and the Haplic Gleysol. The highest pH values were recorded in brook sediments and suspended matter.

Concentrations of Cd continuously exceeded relevant precaution values according to the German Soil Protection Ordinance (BBodSchV 1999: 1578). Mean concentrations and concentration ranges of Cd were roughly similar in all sampled soil types. For the majority of soil profiles, the concentrations of Cd slightly increased with the transition from 0-10 cm to 20-30 cm depth. Brook sediments reached a roughly similar range and mean value as observed for soils within the increment of 20-30 cm depth. The highest mean concentrations of Cd were found in samples of suspended matter (Fig. 3, left side), which reached maximal concentrations at sampling site 2. In all samples, the highest percentages of total concentrations occurred in fractions F1 and F2. Percentages of F1 were lowest in soil samples from 0-10 cm depth and reached similar values in 20-30 cm depth, brook sediments and suspended matter. Percentages of F2 were similar in both sampling increments of soils, whereas slight increases occurred in brook sediments, and suspended matter. Percentages of F3 and F4 were marked by distinct decreases starting in soils (0-10 cm depth) and progressing with the transition to brook sediments and suspended matter (Fig. 3, right side).

Total concentrations of Cu mostly exceeded relevant precaution values (BBodSchV 1999: 1578). Cu concentrations in soils were marked by a high spatial variability, which is expressed in a relatively wide range of the measured concentrations. The highest concentrations were found in Colluvic Cambisols and the Cambic or Colluvic Leptosols of the lower valley section. The lowest concentrations occurred in Dystric Cambisols and the Haplic Gleysol of the upper valley section. Brook sediments and suspended matter were marked by narrow ranges. Cu concentrations in the suspended matter clearly exceeded the contents found in brook sediments (Fig. 4, left side). Fraction 1 constituted the lowest percentages in all samples. Both depth increments of soils showed similar percentages of F2, while amounts of the reducible fraction in brook sediments and the suspended matter were only half as high. Proportions of F3 in soils decreased with increasing soil depth and increased again within the sediment sam-
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The highest percentages of F3 were recorded in the suspended matter, clearly exceeding the other fractions. In all other sample groups, F4 reached the comparatively highest proportions, as it showed the highest percentages in the sample groups (i.e. soil 20-30 cm; brook sediments) with lowest mean total concentrations (Fig. 4, right side).

A distinctive enrichment of Pb was found for all samples. The relevant threshold values were exceeded in the majority of the samples (BBodSchV 1999: 1578). Especially the soils exhibited strong enrichments. Those were extremely high in the Colluvic Leptosol, also, albeit less, in 0-10 cm depth of Colluvic Cambisols and Cambic Leptosols situated in the lower valley.

Table 3  Mean values of particle size distribution, C_org, pH-value, and total concentrations of Cd, Cu, and Pb in the soil, brook sediment, and suspended matter samples (in total 51 samples). Transect soils are grouped in dependence on their soil type, soils with a profile depth < 30 cm (i.e. Colluvic Leptosol) were sampled in 0-10 cm depth only (n = number of investigated soil type and the resultant number of samples taken from a sampling depth; total sample numbers of a soil type in bold numbers). Source: Own elaboration

<table>
<thead>
<tr>
<th>Sample group</th>
<th>Particle sizes (%)</th>
<th>C_org (%)</th>
<th>pH</th>
<th>Cd (mg/kg)</th>
<th>Cu (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dystric Cambisols</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-10 cm</td>
<td>43.9</td>
<td>21.0</td>
<td>31.5</td>
<td>6.56</td>
<td>3.72</td>
<td>2.53</td>
<td>77.9</td>
</tr>
<tr>
<td>20-30 cm</td>
<td>39.1</td>
<td>28.7</td>
<td>32.2</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td>538</td>
</tr>
<tr>
<td>range (all samples)</td>
<td>0.76-11.7</td>
<td>3.38-3.94</td>
<td>1.92-9.34</td>
<td>28.3-118</td>
<td>84.4-3317</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colluvic Cambisols</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-10 cm</td>
<td>42.0</td>
<td>34.2</td>
<td>23.8</td>
<td>10.8</td>
<td>3.53</td>
<td>3.03</td>
<td>119</td>
</tr>
<tr>
<td>20-30 cm</td>
<td>44.8</td>
<td>30.1</td>
<td>25.1</td>
<td>6.36</td>
<td>3.58</td>
<td>4.01</td>
<td>182</td>
</tr>
<tr>
<td>range (all samples)</td>
<td>4.09-12.1</td>
<td>3.43-3.65</td>
<td>2.61-4.21</td>
<td>80.1-190</td>
<td>2844-5855</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colluvic Leptosol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-10 cm</td>
<td>22.0</td>
<td>43.0</td>
<td>35.0</td>
<td>16.9</td>
<td>4.52</td>
<td>11.2</td>
<td>281</td>
</tr>
<tr>
<td>range (all samples)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cambic Leptosols</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-10 cm</td>
<td>44.3</td>
<td>33.7</td>
<td>21.9</td>
<td>4.73</td>
<td>4.68</td>
<td>5.05</td>
<td>466</td>
</tr>
<tr>
<td>20-30 cm</td>
<td>37.1</td>
<td>36.9</td>
<td>26.0</td>
<td>0.95</td>
<td>4.75</td>
<td>3.62</td>
<td>33.8</td>
</tr>
<tr>
<td>range (all samples)</td>
<td>0.54-6.34</td>
<td>3.92-5.55</td>
<td>2.69-7.16</td>
<td>19.1-681</td>
<td>11.2-5523</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Haplic Gleysol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-10 cm</td>
<td>38.0</td>
<td>45.8</td>
<td>16.2</td>
<td>8.51</td>
<td>7.08</td>
<td>4.65</td>
<td>47.5</td>
</tr>
<tr>
<td>20-30 cm</td>
<td>49.6</td>
<td>27.4</td>
<td>22.9</td>
<td>4.00</td>
<td>6.61</td>
<td>3.38</td>
<td>47.9</td>
</tr>
<tr>
<td>(all samples)</td>
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<td>Gleyic Fluvisols</td>
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<tr>
<td>0-10 cm</td>
<td>49.3</td>
<td>30.6</td>
<td>20.1</td>
<td>6.61</td>
<td>5.31</td>
<td>4.36</td>
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<td>20-30 cm</td>
<td>60.0</td>
<td>22.4</td>
<td>17.6</td>
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<td>5.79</td>
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<td>4.41-6.63</td>
<td>2.35-10.2</td>
<td>29.5-920</td>
<td>225-4319</td>
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<td>Brook sediments</td>
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<tr>
<td>0-10 cm</td>
<td>47.5</td>
<td>30.4</td>
<td>22.1</td>
<td>8.39</td>
<td>6.50</td>
<td>4.68</td>
<td>66.8</td>
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<td>6.15-6.65</td>
<td>2.34-7.22</td>
<td>20.9-166</td>
<td>126-1453</td>
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<td>Suspended matter</td>
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<td>52.6</td>
<td>26.7</td>
<td>17.4</td>
<td>6.28</td>
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<td>6.03-6.37</td>
<td>5.32-6.40</td>
<td>50.8-62.0</td>
<td>962-1189</td>
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<td>sampling site 2</td>
<td>11.6</td>
<td>46.7</td>
<td>41.8</td>
<td>21.3</td>
<td>6.26</td>
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<td>6.33-6.18</td>
<td>6.12-11.7</td>
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The effect of catchment soils on heavy metal concentrations in a brook situated in the historic mining region of Braubach, Germany

A correlation analysis was conducted by combining all measured values from soil, sediment, and suspended matter samples. With the exception of correlations existing between the different fractions of an element, only a few significant correlations were found. Significant correlations were observed between pH-value and fractions F1, F2, and total concentrations of Cd. A close relation between Cu and Pb was found for the total concentrations of both elements. A rather weak correlation was also observed between $C_{\text{org}}$ and total concentrations of Pb (Table 4). Further significant correlations were found for F4 of Cu which was positively correlated with sand contents, and negatively correlated with contents of silt and clay.
5. Discussion

The close relation between brook and catchment soils is obvious due to elevated concentrations of the same elements in soils, sediments, suspended matter, and water. An increase of heavy metal pollution within the lower valley section is indicated by comparatively higher concentrations in sampling sites located there. Rising concentrations of dissolved Cd, Cu, and Pb between the sampling sites 1 and 2 reflect a contiguous increasing pollution of soil and water. Due to the presence of the most polluted soils within the lower valley section, an enhanced release of dissolved metals from catchment soils to brook water can be assumed. Hereby, concentrations of dissolved Cd and Pb in water samples increased to a higher factor than dissolved Cu. In the case of Cd, this can be explained by its relatively high mobility in acidic soils (Blume and Brümmer 1991: 166) and the high percentages in F1 and F2 in the soils, brook sediments, or suspended matter, which facilitate the transfer of Cd into the water. The equal rise of dissolved Pb concentrations is, in contrast, only explainable by the high total concentrations of this element within the study area. Although the mobile proportions of accumulated Pb in soils are normally smaller than those for Cd (Liu et al. 2016: 19), its mobility is enhanced by increasing total concentrations (Hornburg and Brümmer 1993: 476). Though the total concentrations of nearly all samples from soils, sediments, and suspended matter show large enrichments of Pb, even the relatively small percentages in F1 seem to be sufficient to enable a severe
increase of dissolved concentrations along the course of the brook. The enrichment of Cu within the study area also enables a release to the water phase. Due to the smaller degree of enrichment in comparison to Pb and a likely higher retention than Cd, the increases of dissolved Cu concentrations are smaller between sampling sites 1 and 2.

With regard to the solid samples, the concentrations of all studied elements reached their highest variability in the soils and comparatively lower ranges in the sediments or the suspended matter. This fact is likely due to mixing processes during fluvial transport dynamics. The element loads of the soils, the sediments, and the suspended matter clearly differ in the case of Cd. An obvious enrichment in brook sediments and suspended matter indicates a flux of Cd from catchment to brook. Due to missing correlations and similar textures of soil and sediment samples, this flux is not solely explainable by differences in clay contents, which can comprise the highest element load within the different grain fractions of soils, sediments, and suspended matters (Helios-Rybicka and Kyziol 1991: 164ff). Although a high Cd concentration in the suspended matter is facilitated by the fine texture, an additional transfer of dissolved Cd from catchment soils to the brook seems obvious. The high dislocation ability of Cd in the soils is indicated by increasing total concentrations with the transition to deeper soil parts and can be explained by the increasing mobility of this element under low pH conditions (Tack et al. 1996: 201ff). In addition, a high mobility of Cd can be assumed by the generally high percentages of F1 in soils, which should mostly influence the pore water quality in the comparison of all extracted fractions (Rao et al. 2008: 292ff). An element transfer between soils and brook is explainable by a Cd transport through pore water. As the discharge generation in headwater catchments can be strongly influenced by lateral subsurface flow paths (Heller and Kleber 2016: 943ff) and the terrestrial soils are situated on steep valley slopes, a slow dislocation of dissolved Cd by seepage water in direction of the valley bottom seems plausible. After reaching the floodplain, dissolved Cd should partly be adsorbed to soil and sediment surfaces under higher pH conditions. This can be assumed due to significant correlations between pH value and F1 (r_S: 0.51) or Cd (r_S: 0.40) total concentrations. The subsequent fluvial separation of suspended transported Cd-bearing fine particles and coarser grained sediments explains the concentration differences of sediments and suspended matter.

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The fact that topsoil (0-10 cm depth) concentrations of Cu and Pb clearly exceed the concentrations analyzed for the increment of 20-30 cm depth, results from a lower mobility of both elements in comparison with Cd under the prevailing pH conditions (Brümmer et al. 1986: 391ff.). In addition, small proportions of F1 are evidence for a relatively high retention for Cu and Pb. Steep vertical gradients between both sampled depth increments indicate that both elements mostly originate from anthropogenic inputs. The widespread enrichment of Cu and Pb in topsoils of terrestrial sites is typical for the atmospheric deposition of heavy metal enriched airborne dust (Pajak and Jasnik 2011: 177; Hernandez et al. 2003: 200ff). An additional mixing with eroded slag heap materials explains the extreme concentrations observed in the Colluvic Cambisols and the Colluvic Leptosol situated in the lower valley section. The distinctively lower total concentrations of Cu in soil increments of 20-30 cm depth and brook sediments, which are connected with simultaneously rising proportions of F4, are likely reflecting an enhanced influence of geology. Although the concentrations of Cu and Pb also clearly exceed their regional geogenic background values (Hauenstein et al. 2008: 44.2) in 20-30 cm depth, the decrease of total concentrations in comparison with 0-10 cm depth should be connected with a declining influence of the atmospheric heavy metal input. Geogenic heavy metals are bound in the crystalline structure of minerals before they are gradually released by processes of rock weathering (Liu et al. 2017: 44). Therefore, geogenic heavy metal amounts in soils normally contain higher residual bound percentages than the amounts of heavy metals, which entered a soil due to anthropogenic activities (Borgese et al. 2013: 5074). Vertically decreasing total heavy metal amounts in combination with rising proportions of the residual bound fraction hence indicate an increase of relatively less weathered or coarser mineral grains and rock fragments.

In comparison with brook sediments, the presence of higher Cu and Pb concentrations in soils evidences a higher retention for both elements as observed for Cd. In contrast to the brook sediments, the comparatively higher total contents of Cu and Pb in the suspended matter are connected to changing proportions of Corg and fine grain sizes. However, as only a rather weak correlation between Corg and total Pb concentrations (r_S: 0.39) was found, the quality of suspended matter seems to be determined by the interaction of further factors. In the case of Cu, the differences in grain size and Corg between brook sediments and
suspended matter clearly influence the percental distribution of oxidizable F3 and residual F4 fractions: On the one hand, comparatively higher proportions of F3 in suspended matter should be connected with simultaneously high amounts of $C_{org}$ and the preferential binding of Cu on organic substances (Hiller and Brümmer 1997: 50). On the other hand, coarser mineral grains contained higher residual fractions than the finer grained material, which is indicated by the positive correlation (rs: 0.50) between sand contents and the F4 fraction of Cu. Anthropogenically released heavy metals are frequently adsorbed on the surfaces of the fine grain fraction of soils or sediments (Yao et al. 2015: 6736). Hence, the fine texture of suspended matter favors declining proportions of F4, whereas coarser mineral grains remaining on the streambed should increase residual amounts of Cu in brook sediment samples.

6. Conclusions

Smelting and mining processes caused a heavy metal contamination in the study area. The relatively high accumulation of Cd, Cu, and Pb in catchment soils enabled an enrichment of these heavy metals in the dissolved element load of brook water. The spatial distribution of heavy metal concentrations in soils differed through variable impacts of potential pollutants and soil formation. Specific differences in element mobility resulted in a slight enrichment of Cd in a soil depth of 20-30 cm and a comparatively higher retention of less mobile Cu and Pb in a soil depth of 0-10 cm. Differences in heavy metal concentrations of the catchment soils, the brook sediments, and the suspended matters showed a higher transfer from soils to brook sediments and suspended matter for Cd than for Cu and Pb. The comparative analysis of samples from soils, sediments, and suspended matters by means of a sequential extraction method revealed distinct changes in binding fractions of Cd or Cu and a relatively consistent sorption of Pb by the reducible fraction. Element-specific mobility is postulated as an important determinant for these processes.

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