Contamination Characteristics of the Confluence of Polluted and Unpolluted Rivers – Range and Spatial Distribution of Contaminants of a Significant Mining Centre (Kutná Hora, Czech Republic)

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Abstract


The study brings new insights into the topic of the contamination characteristics of the mining region of Kutná Hora (Central Bohemia). The previous meta-analysis of the contamination studies showed that there could be a surprisingly low spatial range of contaminated river sediment downstream of Kutná Hora. The study should answer the question as to whether it is justifiable to interpret the presence of contaminants as a result of Kutná Hora mining. There was found a rapid increase in concentrations between the background area and contaminated Kutná Hora. Increase of medians (in mg/kg) of As: 33 and 148, Cu: 34 and 57, Pb: 35 and 82, Zn: 85 and 232; means increased ca 10 times. Then a decrease between the contaminated area and the confluence area was observed. But this decrease was influenced by the presence of extreme values in the contaminated area and therefore it was observed only in means. Medians of the elements concentrations did not decrease. The concentrations of the elements decreased after the confluence to lower values, but they stayed at the contaminated area levels. The background levels were observed only in the probes related to Labe alluvium. But also in these probes, the contamination was traced by multivariate analyses – by clear separation of As, Cu, Pb, Zn from other elements. The contamination was manifested in probes after the confluence mainly in the topsoil levels of alluvium, ca. in 10 to 40 cm. The original starting point of this study, that the contamination is not firmly manifested in the areas after the confluence, based on meta-analysis of regional studies, is not valid.

Keywords: 3D analysis; magnetic susceptibility; pollutant distribution; river sediments; spatial analysis; trace elements

Many studies concern rivers and their alluvia as an important environment for both transport and the storage of metal contaminants (e.g. Macklin & Klimek 1992; Brewer & Taylor 1997; Miller 1997; Bird et al. 2005; Raab et al. 2005; Ettler et al. 2006; Knox 2006; Hilscherová et al. 2007; Taylor & Owens 2009; Martin 2015). The storage can be long term (Tylecote 1987; Grattan et al. 2007). Floodplain storage can be changed into a contamination source, e.g. by its erosion (Gäbler & Schneider 2000; Coulthard & Macklin 2003; Craddock & Lang 2003; Förstner et al. 2004; Hürkamp et al. 2009a). Some studies focus on contamination distribution in both horizontal and vertical dimension, but they are few (e.g. Park & Vlek 2002; Dennis et al. 2009; Hürkamp et al. 2009b). The region of Kutná Hora was a significant centre of mining and smelting (especially from the 13th to the 16th century – see Kořan 1950; Bartoš 2004) and therefore it is strongly contaminated, mainly by As, Cu, Pb, and Zn. These contaminants can be divided into subgroups of As, of Cd, and of Cu, Pb and Zn.
with different spatial patterns and probably different source of mining and smelting activities (Králová et al. 2010; Vondráčková et al. 2013; Ash et al. 2014; Horák & Hejcman unpublished study). This source of contamination also lies in the proximity of the Labe River – the main river of Bohemia flowing through an intensively inhabited and agriculturally used region. The Labe River is variably contaminated along the stream (Borovec 1995), which is also interpreted as a result of Kutná Hora mining and smelting activities (Veselý & Gürtlerová 1996). The meta-analysis of the contamination studies from Kutná Hora (soil samples, values obtained by HNO₃ solution) showed that there are probably very low values of the contaminants in the confluence area of the Klejnárka and Labe Rivers (Horák & Hejcman unpublished study). This study was focused on this confluence area. The aims were to specify: (1) if there is a detectable Kutná Hora contamination signal after the confluence of the Klejnárka and Labe Rivers, (2) if there is a change in the character of the contamination, (3) if there are changes in the contamination distribution in horizontal and vertical directions.

**MATERIAL AND METHODS**

**Study area.** We studied the area of the confluence of the Klejnárka River and the secondary channel of the Labe River (called Černá strouha – “Black gutter/drain”) and then the main channel of the Labe River (Figure 1; geographical coordinates: 50°0’44.152”N, 15°16’49.725”E). The Klejnárka River is the main drainage river of the Kutná Hora mining and smelting area. There was no outstanding historical mining centre in the Labe River catchment. There was some mining activity e.g. in the Krkonoše Mts (ca. 15–19th century), but nothing comparable to Kutná Hora. Also the previous study (Horák & Hejcman unpublished study) revealed that there should be no contamination comparable in Labe environment.

The geological background of the confluence area mostly comprises Mesozoic rocks, Pleistocene and Holocene Aeolian and river sediments. All the probed sites are located in the Holocene alluvial sediments. The soil cover mostly comprises Fluvisols, minor representations of Chernozems and soil formed by gleyic processes. The probed sites are in arable land; the neighbouring areas are covered by Pinus sp. forests. The geologic and natural background of the Kutná Hora area is made partly of Palaeozoic or Precambrian rocks (gneiss of various types) and partly of Mesozoic rocks (marlstones, siltstones). The soils are represented mainly by Cambisols.

**Research design.** Soil samples were taken in the area of fluvial sediments of both rivers. Only the arable land was probed. There were also forest areas, but mostly elevated and sandy (aeolian sand dunes) and no other land cover area was in the confluence area (Figures S1–S3 in electronic supplementary material (ESM); for the supplementary material see the electronic version). We made 25 vertical probes with Ejkelkamp soil probe (Figures 1, S1–S3 in ESM). Each probe contained one main probe and two sub-probes at a 1 m distance to eliminate random divergences (i.e. we made 75 drilled cores totally). We sampled the soil every 10 cm to the depth of 80 cm.
The majority of samples came from silty to silty/loamy sediments. We also took samples in Kutná Hora town to obtain data from the contaminated area – topsoil and archaeological sediments. We also sampled the areas of probably no human induced contamination (“background”) from the topsoil, colluvial and alluvial sediments.

**Analysis methods.** All the sampled material was air dried. Only fraction under 2 mm was then analyzed. All measurements were performed by a portable ED-XRF spectrometer (Innov X Delta; Innov-X Systems Inc., Woburn, USA) to obtain near-total concentrations (for application of XRF spectrometry see Piorek 1997; Clark et al. 1999; Kalnicky & Singhvi 2001; Hürkamp et al. 2009b). The quality of the device measurements was successfully tested by BAS Rudice Ltd. (www.bas.cz) on 55 reference materials (e.g. SRM 2709a, 2710a, 2711a, OREAS 161, 164, 166, RTC 405, 408). All the samples from the confluence area were analyzed on the Kappabridge Kly-2 (Agico, Brno, Czech Republic) to obtain magnetic susceptibility (laboratory of the Department of Geology, Faculty of Science, Palacký University in Olomouc), which has been used as a contamination marker or tracer (Hilscherová et al. 2007; Bábek et al. 2008, 2011). Only part of the material from each sample (by sample we mean sampled sediment from one site and depth) was measured three times; in the case of unusual value one additional part from the sample was measured. In some cases from the confluence area, there was also no or little usable material from sampled depth due to hiatus or coarse material (e.g. no samples from probe 3, depth 80 cm). Arithmetic mean of each part measurements was used in all the following analyses. The number of measured sample parts in analyses input data (i.e. number of data points) was 645 for confluence, 85 for contaminated area, and 52 for background. For the confluence area interpolations it was a mean from the means of main probe and two subprobes spatially related to main probe.

For the analyses, we used only magnetic susceptibility and As, Cu, Pb, and Zn as these are the elements representing Kutná Hora contamination (Horák & Hejcman unpublished study). These were the main Kutná Hora contaminants successfully measured by ED-XRF – i.e. above the limit of detection. Due to this limit, we were not able to analyze Cd concentrations. For multivariate analyses we used these elements: Al, As, Ca, Cu, Fe, K, Ni, P, Pb, Rb, Si, Sr, Ti, V, Zn, Zr, and LE (which stands for “light elements”, i.e. all elements lighter than Mg combined) to build a matrix. We have chosen these elements due to their high number of successful measurements (above detection limit). We used boxplots for the assessment of relations of data among the background, the contaminated and the confluence areas. For more detailed analyses and for better presentation we also divided the probes from the confluence areas into three groups (high, middle, lower) in rough accordance to median values of As, Cu, Pb, and Zn together (Figure 1). The boxplots were based on the concentrations and on the enrichment factors of the elements normalized to Al concentration. Normalized values of each sample part were divided by a mean of background normalized values. For detailed analysis of the confluence data, we used mainly multivariate analyses (principal component analysis (PCA) and factor analysis (FA)) of the data after clr (centered log-ratio – for details please see below) transformation and GIS kriging interpolation. PCA was used mainly to obtain eigenvalues as the basis for the FA design. FA was used for its suitability for easier interpretation of results, yet the PCA results were presented as well.

The clr transformation was performed according to Reimann et al. (2008). This transformation is based on the division of element concentration by a geometric mean of the data point and then on logarithmic transformation of the resulting value. This processing is suitable for the geochemical data, since they are of compositional nature. The multivariate analyses were performed also on the data subsets of high, middle, and lower probes, respectively. For interpolations, we used ordinary kriging method with a spherical variogram model (for more specifications based on Geostatistical wizard function of ArcGIS 10.1 see Figure S21 in ESM). For visualization of the interpolated raster we used geometric intervals and 12 classes. Beside ArcGIS 10.1, also STATISTICA v.10 and R 3.1.2 (R Core Team 2014) software was applied.

**RESULTS**

Multivariate analyses extracted the contamination elements (As, Cu, Pb, and Zn) standing separately in the elemental complex of the confluence area. PCA did not extract this separation in the analysis of the high probes data only. Factor analysis extracted this separation in all cases (for the results see Figure S22 in ESM). The division of the contamination elements
Figure 2. Boxplots of As concentrations on gradient background area – contaminated area – probes of confluence area; probes are sorted in accordance to high, middle, and lower probes and then ascending; numbers in italics represent number of data points (sample parts) in input data for each box; values are in mg/kg; boxplots indicate median, 25th and 75th percentile, thresholds for outliers (circles) are stated as 1.5 of box height; boxplots for As, Cu, Pb, Zn, and magnetic susceptibility for all depths (Figures S4–S9 in ESM)

Figure 3. Visualization of the spatial diversity of clr-transformed values of As and Cu; probes symbolization is the same as in Figure 1b
into subgroups was not extracted. The scatterplots of magnetic susceptibility and the contamination elements did not show any clearly strong relation (Figures S19 and S20 in ESM). The boxplots of elements values on gradient background – contaminated – confluence areas (Figure 2 and Figures S5–S9 in ESM) revealed the highest values in the contaminated area. The high probes data was generally in accordance to the contaminated area. The values after the confluence of the Klejnárka and the Labe secondary channel decreased. The values at the deeper levels of alluvium were more variable then the values in the topsoil. The boxplots analyses of enrichment factors have brought similar results to those of concentrations (Figure S4 in ESM). The interpolation revealed this general pattern: concentrations were mostly manifested by high values in the area on the left bank of the Klejnárka above the confluence. The values decreased under the confluence, but stayed manifested along the channel mainly in the topsoil levels. Interpolations of clr transformation values have shown that there was some manifestation of the elements also in the deeper levels, e.g. at 80 cm of probes 21 and 23 (Figures 3 and 4 and Figures S10–S18 in ESM).

**DISCUSSION**

We interpreted the results of multivariate analyses as a prove of the Kutná Hora contamination manifestation in the area of the confluence. The absence of division into sub-factors was interpreted as a result of mixing of the contamination sub-factors by transport (but there was no special research done on the topic of the main medium of transport). The contamination diversity in Kutná Hora was also based on spatial relation to particular areas of Kutná Hora – the factor naturally not acting in the confluence area – the contamination should be mixed here without relation to transport media. We observed the decrease of values between the contaminated and the confluence areas (Figures 2 and S4–S8 in ESM). There were no values such as outliers or extremes in the confluence areas. Table 1 showed, that only means of concentrations decreased in a majority of contaminated-confluence couples. Outliers and extremes had strong influence on the contaminated mean value. By medians, a majority of the sample parts from the contaminated and the confluence areas reached similar or even higher values in the confluence area. Therefore, the only dif-
ference would be the presence of outliers and extreme values in the contaminated area. The strong influence of extreme contaminated values was observed also in the increase between the background and the contaminated areas – medians increased ca. 2–5 times, means increased ca. 10 times. It could also be the result of the presence of non-contaminated (and sampled) sediments in the contaminated area of Kutná Hora town. The values of the contaminated area could be, for example, compared to those published recently by Ash et al. (2014) from a slag heap to the south of Kutná Hora. The As reached ten to hundred times lower values than older samples from Kutná Hora, Pb was of similar values and Cu and Zn were higher.

The major pattern in the confluence area itself was the decrease after the confluence of the Klejnárka with the Labe secondary channel (difference between high and middle probes). We interpreted this as a result of dilution of the contaminated water and stream load of Klejnárka River by its mixing with unpolluted wa-

ter and stream load of Labe River. This decrease and change was more distinctive at deeper levels: from 40 to 80 cm. The manifestation of the contamination in the area after the confluence was observed more in the topsoil levels (ca. from 10 to 40 cm). We would interpret the low values probes as the Labe environment, uninfluenced by the contaminated Klejnárka water as concentrations were of comparable values to background values. But, performing PCA and FA on probes sub-datasets (Figure S22), we have also found a contamination factor in the Labe alluvium environment (lower probes). Also, the clr transformed data enabled the interpretation of deeper levels interpolations, where only the concentrations were not easy to interpret due to unsuitable variograms. A fine manifestation at a 80 cm depth in probes 21 and 23 (Figures S10, S12, S14, S16 in ESM) was observed. The magnetic susceptibility spatial distribution was generally the same, but the correlation between it and the elements was not convincing (Figures S19 and S20 in ESM).

Table 1. Main characteristics of concentrations of As, Cu, Pb, and Zn (in mg/kg)

<table>
<thead>
<tr>
<th>Area</th>
<th>Count</th>
<th>Max</th>
<th>Mean</th>
<th>Median</th>
<th>Min</th>
<th>MAD</th>
</tr>
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<tbody>
<tr>
<td>background</td>
<td>158</td>
<td>159</td>
<td>40</td>
<td>33</td>
<td>10</td>
<td>16.31</td>
</tr>
<tr>
<td>contaminated</td>
<td>306</td>
<td>24 753</td>
<td>581</td>
<td>148</td>
<td>13</td>
<td>117.87</td>
</tr>
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<td>357</td>
<td>140</td>
<td>135</td>
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<td>37.06</td>
</tr>
<tr>
<td>middle probes</td>
<td>586</td>
<td>285</td>
<td>94</td>
<td>87</td>
<td>8</td>
<td>16.31</td>
</tr>
<tr>
<td>lower probes</td>
<td>857</td>
<td>103</td>
<td>31</td>
<td>31</td>
<td>4</td>
<td>10.38</td>
</tr>
</tbody>
</table>

| background    | 148   | 68      | 34   | 34     | 12  | 11.86 |
| contaminated  | 293   | 3 167   | 264  | 57     | 18  | 40.03 |
| high probes   | 637   | 298     | 152  | 155    | 34  | 32.62 |
| middle probes | 583   | 226     | 102  | 108    | 13  | 20.76 |
| lower probes  | 778   | 92      | 33   | 32     | 11  | 8.90  |

| background    | 158   | 79      | 37   | 35     | 13  | 14.83 |
| contaminated  | 293   | 4 744   | 428  | 82     | 12  | 94.89 |
| high probes   | 638   | 528     | 256  | 254    | 40  | 60.05 |
| middle probes | 586   | 403     | 160  | 166    | 8   | 22.24 |
| lower probes  | 860   | 119     | 37   | 36     | 7   | 11.86 |

| background    | 158   | 333     | 94   | 85     | 25  | 31.13 |
| contaminated  | 302   | 19 140  | 1 425| 232    | 23  | 246.85 |
| high probes   | 638   | 1 548   | 627  | 605    | 101 | 151.97 |
| middle probes | 586   | 2 186   | 490  | 449    | 30  | 134.92 |
| lower probes  | 868   | 386     | 116  | 108    | 14  | 35.58 |

Bold values mark those cases, where we found decrease from contaminated to confluence area; high, middle, and lower probes indicate probes of confluence area; MAD – median absolute deviation (we used this parameter following recommendations by Reimann et al. 2008)
Hürkamp et al. (2009b) found that the decrease in the contaminants needs not be correlated with the distance from the stream; Brewer and Taylor (1997) found that palaeochannels could be more contaminated than floodplains. We found similar patterns to the findings of Hudson-Edwards et al. (1996): the decrease in the contamination was probably caused by the dilution of the contaminated water, transported material and sediment after the confluence. As it was presented in some of the previous studies (Vešelý & Gürtlerová 1996; Horák & Hejcmans 2013), vertical trends in the Kutná Hora region can record outstanding peaks or diversity. The trends found in the probes of the confluence area recorded no outstanding peaks (compare values for every probe on Figures S9–S13 in ESM). Vertical developments have been published e.g. by Nováková et al. (2013): both the values of Pb concentration and of magnetic susceptibility increased in the published profiles. The increase was interpreted as a result of continual pollution in the recent decades. A similar situation was observed by Hürkamp et al. (2009a) – the highest values in the topsoil – or by Ciszewski et al. (2012) – vertically diversified values, which were partially caused by different profile environments (stream channel, floodplain, fish pond). Vertical differences were also found in the studies of Ciszewski (2003), or of Lecce and Pawlowsky (2001). Usually, the contamination peaks, interpreted as a result of anthropogenic activities, were bound with similar elements as in our study – Pb, Cu, Zn (Hindel et al. 1996; Matschullat et al. 1997).

We did not find such a situation – i.e. the opposition to the previous findings from St. Anne’s fish pond or Mlady Hlízov, sites in the Klejnárka floodplain closer to Kutná Hora, with differences in the vertical development (Horák & Hejcmans 2013). The absence of distinctive peaks could be interpreted as a result of an inactive contamination source in the Kutná Hora region at the time of sedimentation of these alluvial layers. Or, the contamination was homogenized during transport and sedimentation.

CONCLUSIONS

The contamination coming from Kutná Hora (represented by As, Cu, Pb, and Zn) can be traced in the area of the confluence of the Klejnárka and Labe Rivers. By the concentration values and by contaminants ratios to normalizing elements, this contamination can be traced mainly in the nearness of the channel. But in the Labe alluvium environment (lower probes) it can be traced not by concentrations, but by multivariate analyses. The contamination was more manifested in the topsoil levels, but the clr transformed data helped find finer manifestations at deeper levels, too. It was revealed that the original starting point of the study, that the contamination was not manifested in the areas after the confluence (based on meta-analysis of regional studies), was not valid.

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