Mulde River - A Uranium Mining Archive

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Abstract. River sediments are archives for past water contaminations. This is shown for the catchment of the Mulde River draining major parts of the Erzgebirge, Saxony, Germany. Mining activities have been impacting this part of Germany for over 850 years. It started with silver, then changing to lead, cadmium, zinc, tin, tungsten and copper. Finally, after 1945 a big uranium boom took place in this area which was led by the Soviet Union and the company SAG Wismut / SDAG Wismut, respectively. Until 1990 this area and parts of Thuringia produced 231,400 t of uranium and for this time period made the GDR the third biggest uranium producer of the world. Field work in 2011 revealed that both water and sediments still contain significant concentrations of uranium, cadmium, zinc, arsenic and other mining-related elements. Factor and cluster analysis has been used to visualize the data. Certain areas such as the former Freiberg mining area are high in lead, arsenic and cadmium but low in uranium. On Contrary, those areas where uranium ore was mined still show high uranium concentration in both water and sediments.

Introduction

The Erzgebirge is a tectonic structure stretching NE-SW exposing Variscian crystalline basement and is part of the Bohemian Massif. It contains various ore deposits in granitic rocks and phyllits. For understanding the formation and evolution of the manifold ore bodies Tischendorf (1986) gives a good overview. The catchment has a size of 7600 km^2 and the elevation ranges from 1244 to 56 (m.a.s.l.) at the discharge point to the Elbe River.

Mining for silver and later for zinc, lead, cadmium and other elements took place in the Erzgebirge since the 11th century. Besides mining activities, smelters and small- and medium-sized metal industry over centuries produced waste which was often discharged to the Mulde River and its tributaries. This had already been recognized by Agricola (1556). Uranium was mined around the 1900s in rather small

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quantities for the production of uranium glass in particular in the region of Jáchymov (Sankt Joachimsthal, Czech Republic). This rapidly changed in 1945 when after WW II the Soviet Union started mining uranium in the Erzgebirge. The SAG Wismut was founded in 1947 and renamed to SDAG Wismut in 1954. Until the early 1960s uranium mining, milling and processing was done in many places. Environmental issues had not been considered at all leading to severe environmental contamination by means of spills and dam failures. After 1960 the Wismut SDAG focused on a few big mines (deep and open pit mines) and did the treatment in two centralized milling and treatment plants (Seelingstädt and Crossen). Step by step at least certain environmental protection measures were implemented. With the unification of West and East Germany uranium mining was terminated officially at the end of 1990. SDAG Wismut was reconstructed as Wismut GmbH (owned by the Federal Republic of Germany) and is responsible for the restoration and environmental cleanup of the former mining and milling sites.

Beuge et al. (1999), Kluge 1997 and Hoppe (1995) investigated river sediments of the Mulde River in 1992 and found that the Mulde at that time was by far the biggest contributor to arsenic and metals loads to the Elbe River and the North Sea. Further Investigations with respect to transport and accumulation of metals were performed in the Mulde catchment by Geller et al. (2004).

Methods

Sediment and water samples were taken during November 2011 (Fig. 1). Sediments were taken by a liner or a grabber from the riverbed. In most cases one representative sediment sample was created by mixing over the entire depths; only in some cases sampling and analysis by RFA was performed depth depending. For RFA analysis only the fraction <63 µm was used. The determination was performed with a SPECTRO XEPOS (Bruker) using a standard multi-element calibration procedure. Water samples were taken from the surface of the rivers. Samples for ion chromatography (IC) and ICP-MS were filtered with poly-carbonate filters (200 nm, Sartorius). Samples for ICP-MS were acidified with 1 mL supra pure HNO_3 prior to determination with an X Series 2 (Thermo Scientific) using PlasmaLab version 2.5.9. Calibration was done by external multi-element standards and internal standards (germanium, rhodium, and rhenium). Some elements were read in the direct mode, others with the KED mode (Kinetic Energy Discrimination). An 881 Compact IC pro (Metrohm) was used for determining anions. Cations were determined with an 850 Professional IC (Metrohm).

Evaluation of the data was performed by means of cluster and factor analysis using the public domain Excel add-on XLSTAT and the open source program PSPP. In cases of more than 30% missing values, the parameter was excluded from cluster and factor analysis. In all other cases missing values were replaced by appropriate values (median, detection limit multiplied by 0.5 etc.).

For further statistical evaluation all parameters and element concentrations that were rated to be relevant were tested for normal distribution. The check was carried out both by subjective evaluation of the graphical representation of the histogram, as well as by checking with the Kolmogorov-Smirnov distribution test. Only pH, electrical conductivity and nitrate in water were normal distributed. The sediment data was not normal distributed. Therefore the logarithm of the readings was taken and re-checked with Kolmogorov- Smirnov test. Transformed or untransformed data was used depending on which data showed the greater significance. For the trace elements the logarithmically transformed data was always given preference.

To avoid an impact by different scales data was standardized by means of the following equation.

$$z_{ij} = \frac{x_{ij} - x_i}{s_i} \text{xij}$$

x_{ij}	value i of sample j
x_i	mean of variable i from all samples
si	standard deviation of variable i from all samples
zij	standardized value

After performing the main component methods VARIMAX Rotation was applied and factor scores were calculated.

With respect to cluster analysis Ward´s-method was found to be most suitable for the data given.

Fig.1. Sampling points in the Mulde River catchment. SW = Schwarzwasser, LB = Lungwitzbach, ZM = Zwickauer Mulde, FM = Freiberger Mulde, ZSCH = Zschopau, VM = Vereinigte Mulde (Nestler 2012)

Results

Fig. 2 displays the uranium concentrations in river sediments of the Mulde catchment area. Significantly elevated concentrations of up to 130 mg/kg were found in the sediments of the Zwickauer Mulde and Schwarzwasser which drain the area of the former uranium mining and milling area. On the contrary the Freiberger Mulde which drains the huge Freiberg mining area has sediments with very low uranium concentrations in the range of natural geogenic sediment concentrations (<1 to 10 mg/kg).

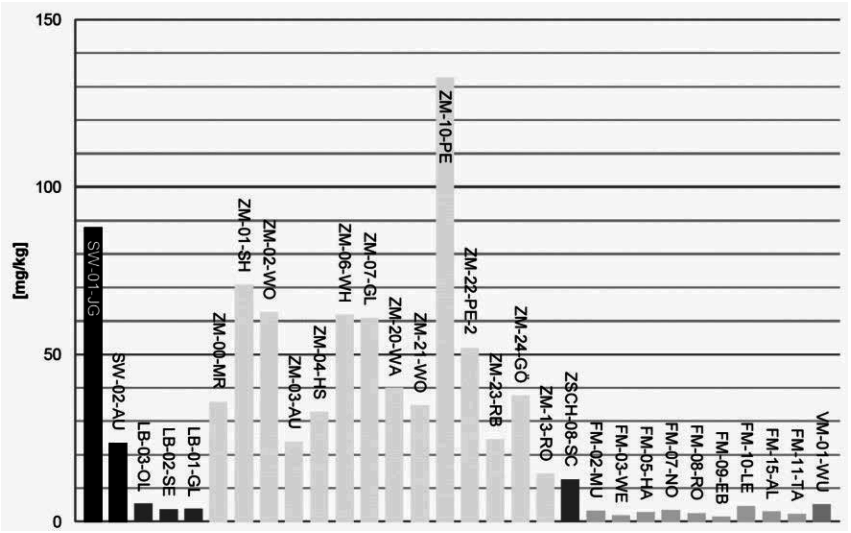

Fig.2. Uranium content in sediments of the Mulde River and tributaries. SW = Schwarzwasser, LB = Lungwitzbach, ZM = Zwickauer Mulde, FM = Freiberger Mulde, ZSCH = Zschopau, VM = Vereinigte Mulde. (Nestler 2012)

However, if one looks at cadmium (Fig. 3), lead and arsenic (the latter two elements not shown here) these elements are significantly elevated in the Freiberger Mulde especially in the vicinity of the city of Freiberg. Here all mines have been closed in 1969 after 850 years of mining activities.

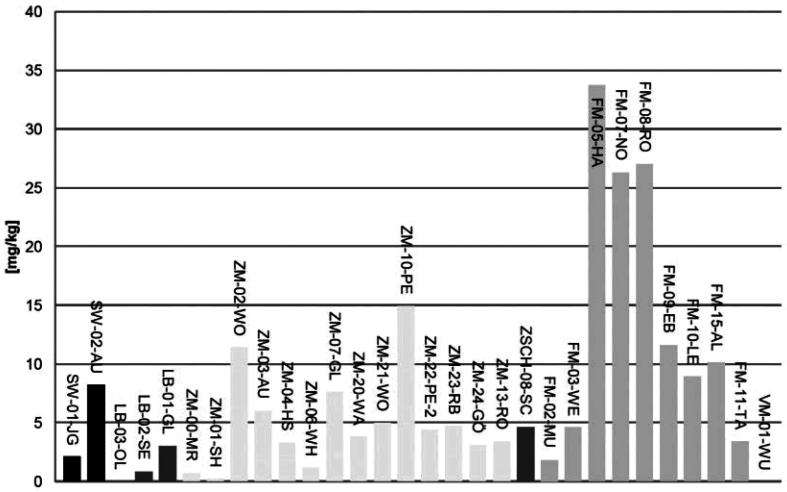

Fig.3. Uranium content in sediments of the Mulde River and tributaries. SW = Schwarzwasser, LB = Lungwitzbach, ZM = Zwickauer Mulde, FM = Freiberger Mulde, ZSCH = Zschopau, VM = Vereinigte Mulde (Nestler 2012)

Fig 4 shows a significant difference for the uranium contents in the Zwickauer Mulde sediment taken in 1992 and 2012. With one exception (ZM-02-WO) the uranium concentrations were more than halved over a period of 20 years.

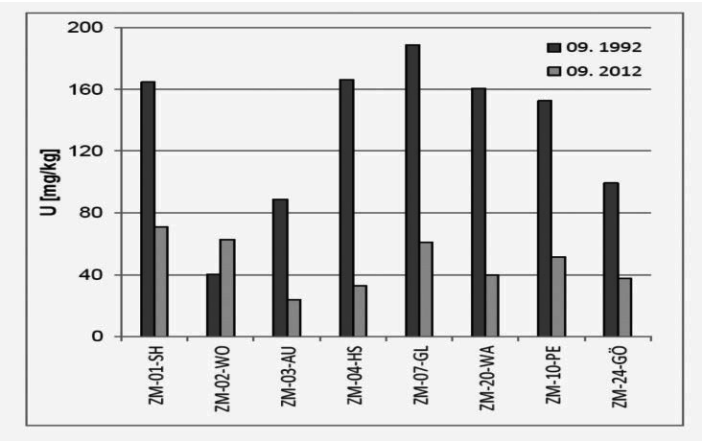

Fig.4. Uranium content in Zwickauer Mulde sediments in 1992 (data from Beuge et al. (1999)) and 2012 (Nestler 2012)

Fig. 5 shows that if one looks at greater depth still significantly elevated uranium concentrations can be found. This is an evidence for the high contamination load during the uranium mining activities in the 1950s, 1960s and 1970s. It is rather

likely that the high concentrations in the sediments will be eluted over time and therefore the water in the Zwickauer Mulde will have significant uranium concentrations for decades.

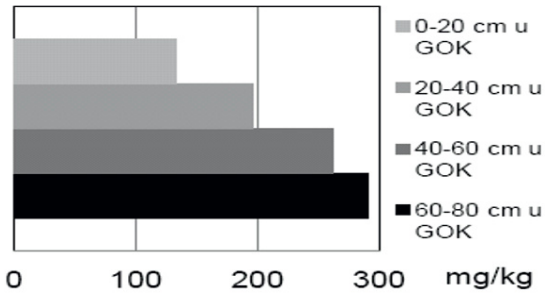

Fig.5. Depth distribution of uranium concentration below surface at the sampling site in Penig (ZM-10-PE) showing an increase with depth. (Nestler 2012)

Table 1 and Table 2 show the factor loadings 1 to 4 and 5 to 7 respectively of water chemistry parameters after VARIMAX rotation.

Table 1: Factor loading of water chemistry data after Varimax rotation; V= variance

Variable	Factor 1 V=46.86%	Factor 2 V=18.65%	Factor 3 V=10.29%	Factor 4 V=6,76%	Communality
ln (Cr)	0.236	0.324	0.594	-0.002	0.513
ln (Mn)	0.087	0.671	0.446	-0.428	0.840
ln (Fe)	-0.795	0.136	0.419	-0.124	0.842
ln (Co)	0.212	0.709	0.469	-0.041	0.769
ln (Ni)	0.175	0.123	0.780	0.309	0.749
ln (Cu)	-0.011	0.591	0.222	0.600	0.759
ln (Zn)	0.169	0.919	0.019	0.053	0.877
ln (As)	0.192	0.093	0.254	0.813	0.771
ln (Cd)	0.103	0.921	-0.115	0.070	0.876
ln (Pb)	0.054	0.840	-0.050	0.230	0.765
ln (U)	0.155	-0.392	**0.782**	0.174	**0.820**
ln(Na)	0.775	0.305	0.287	0.154	0.800
ln(K)	0.863	0.209	0.311	0.016	0.886
ln(Ca)	0.958	0.120	0.080	0.054	0.942
ln(Mg)	0.890	-0.027	0.199	0.017	0.833
ln(Cl)	0.884	0.269	0.195	0.115	0.905
NO_3	0.932	0.119	-0.166	-0.066	0.915
ln (SO_4)	0.887	0.206	0.269	0.031	0.903
ln (HCO_3)	0.946	0.028	0.179	0.022	0.929
ln(PO_4)	0.666	-0.307	0.284	-0.233	0.673
pH	0.822	0.019	-0.062	0.409	0.847

LF	0.920	0.190	0.244	0.083	0.949

Table 2: Factor loading of sediment data after Varimax rotation; V= variance

Variable	Factor 5 V=33.64%	Factor 6 V=28.98%	Factor 7 V=15.55%	communality
ln (Cr_s)	0.083	-0.137	-0.950	0.928
ln (Mn_s)	-0.027	0.779	0.244	0.667
ln (Fe_s)	0.217	0.866	-0.152	0.821
ln (Co_s)	-0.211	0.727	0.024	0.574
ln (Ni_s)	0.140	0.507	-0.795	0.909
ln (Cu_s)	0.853	0.162	-0.298	0.844
ln (Zn_s)	0.866	-0.074	-0.167	0.783
ln (As_s)	0.857	0.167	0.280	0.841
ln (Cd_s)	0.733	-0.088	-0.220	0.594
ln (Pb_s)	0.858	-0.417	0.197	0.949
ln (U_s)	-0.072	**0.774**	-0.293	**0.690**

Fig.6 (left part) displays a result of the factor analysis after VARIMAX rotation. The following parameters were used as variables: pH, electrical conductivity, concentrations of HCO_3^-, Na^+, Ca^{2+}, K^+, Mg^{2+}, Cl^-, NO_3^- SO_4^{2-}, PO_4^{3-}, Fe, Mn, Co, Cu, Zn, As, Cd, Pb, Cr, Ni and U in water. Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Pb and U in the sediment was used as well but is not shown here.

The yellow marked parts of the Zwickauer Mulde are impacted by uranium, nickel, and chromium in water. The occurrence of these elements is due to different sources source, although, this sources are spatially close toeach other. Occurrence of uranium is mainly the result of uranium mining of the SDAG Wismut. Significant positive factor loadings are recorded for the Zwickauer Mulde from Aue, the Schwarzwasser and the Schlemabach (Fig.7). Uranium mining in the 50´s and 60´s under city of Johanngeorgenstadt felt is the reason for elevated uranium content in the Schwarzwasser creek. The former uranium mining provides as well elevated arsenic concentrations of the river. However, a correlation of arsenic and uranium could not be identified. It is assumed that the elevated uranium and arsenic concentrations of the Zwickauer Mulde are not necessarily due to a common source. Factor 2 represents large parts of the Freiberger Mulde where other ore type prevails. Factor 1 interacts with a variance of 46.9% with the exception of the river headwaters in almost all samples (positive factor values). Factor 1 represents those parts of the rivers in the catchment where the major cations and anions in the river water are dominant. Fig 6 (right) shows the result of cluster analysis with the same set of data (water chemistry). The pattern of clusters 1 to 4 is rather similar to that of factor analysis. As well the variables that dominate the 4 factors and the 4 clusters respectively are very similar. This proves that both statistical techniques may be used to evaluate the water chemistry in river systems. Factor and cluster

analysis performed for sediment samples showed very similar results but are not displayed here.

Investigating water and sediments in the catchment of the Mulde River showed that river sediments are meaningful archives for past industrial use and in particular mining activities. The water quality is even after decades of mine closure still significant affected. This is on the one side caused by high concentrations of certain elements in the river sediments and drainage of contaminated mine water from abandoned mines.

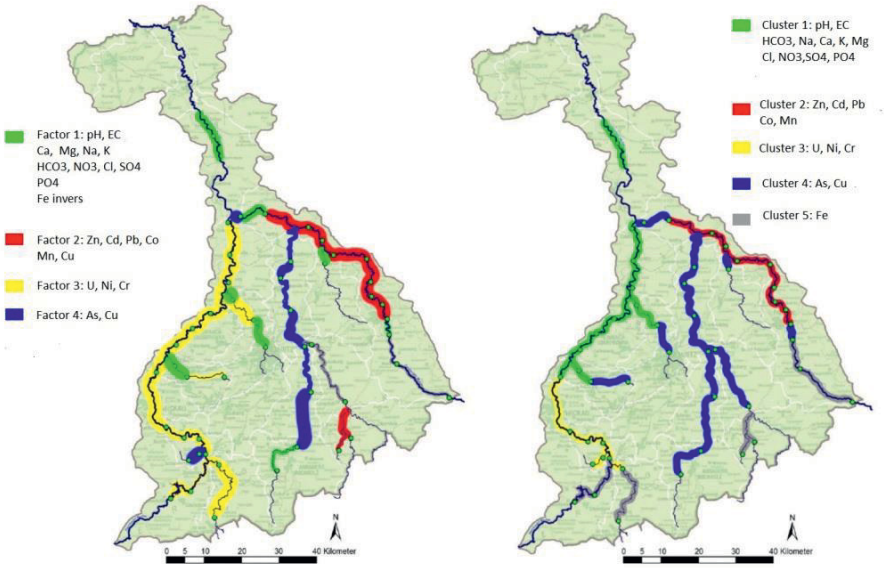

Fig.6. Comparison of factor (left) and cluster (right) analysis for water samples. Both multiple parameter techniques give rather similar results. Factor 2 and cluster 2(red) is dominated by Zn, Cd, Pb, and Mn and show the impact on water quality in the Freiberger Mulde while factor 3 and cluster 3 (yellow) dominate the Zwicker Mulde with the elements U, Ni and Cr. (Nestler 2012).

The highest contaminations of sediments and thus as well factor scores were found in the mining and processing region of Freiberg where the elements As, Cd, Pb, Zn, and Cu prevail. On contrary miainly U and As were found to be elevated in sediments in the area of former uranium mining and processing (Aue, Niederschlema, Hartenstein, Crossen) within the Zwickauer Mulde catchment.

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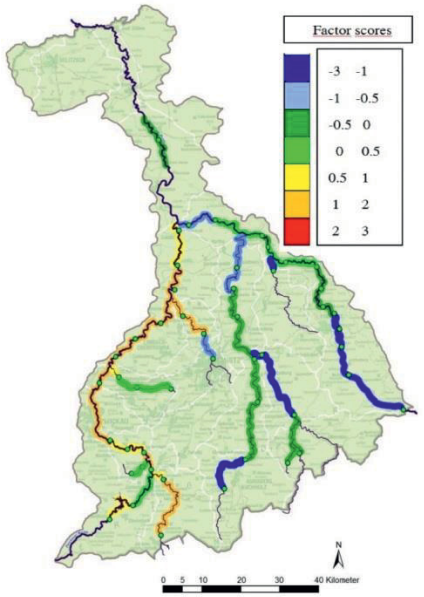

Fig.7. Factor scores for factor 3 (U, Ni, Cr) showing high concentration for water of the Zwickauer Mulde (Nestler 2012)

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