J Radioanal Nucl Chem (2010) 286:367–372
DOI 10.1007/s10967-010-0767-2

Uranium in water of the Mulde River

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Received: 27 July 2010 / Published online: 21 August 2010

Abstract The Mulde River is a left side tributary of the Elbe River and mainly situated in Saxony. The river system consists of the Freiberger Mulde River and the Zwickauer Mulde River, which merge to form the Vereinigte Mulde River. The Zwickauer Mulde River drains the former uranium mining and milling areas in Saxony. This research project was established to quantify the long-term effect of the former uranium mining and milling activities by investigating the content of uranium of the water of the Mulde River. The activity concentration of uranium in samples from the Zwickauer Mulde River is still high compared with the natural background. The values measured in the water of the Vereinigte Mulde River are also elevated, but to a lesser extent due to the dilution effect caused by the merging with the uncontaminated Freiberger Mulde River. Furthermore, the level of contamination of the river water decreased by at least a factor of three as compared to the early 1990s.

Keywords Mulde River · Uranium · Water · Uranium mining · Saxony

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Introduction

At the time of the Warsaw Pact, the former German Democratic Republic (GDR) was the third largest producer of uranium in the world and the most important supplier of uranium for the USSR. The Zwickauer Mulde River in Saxony and the Weiße Elster River in Thuringia are the most important river systems draining the uranium mining and milling dominated areas of the western Ore Mountains and its foreland, resulting in accordingly high heavy metal loads. Thus, they are of particular interest for radiation protection and radioecology. Today, this area is subject to a remediation project which, due to its large scale, can be characterized as pioneer work.

The Mulde River is a left side tributary of the Elbe River and mainly situated in Saxony. The river system consists of three main rivers: Zwickauer Mulde, Freiberger Mulde and Vereinigte Mulde. The Muldenberg Reservoir in the western Ore Mountains is deemed to be the source of the Zwickauer Mulde River. Four kilometers downstream of the dam, which is used as a drinking water reservoir, the river already receives contaminated water from the mine Schneckenstein. On its way through the Ore Mountains the river flows through the uranium mining area Aue and Bad Schlema. Downriver of Zwickau the Zwickauer Mulde River passes Crossen and its uranium ore processing plants and merges with the Freiberger Mulde River at river kilometer 163. The source of the Freiberger Mulde River is located in the Czech Republic, about 5 km from the German border on the ridge of the eastern Ore Mountains. It drains mining areas, however, there is no uranium mining in its catchments area. The Vereinigte Mulde River, which is often simply called Mulde River, originates from the merging of the two frontal flows Freiberger Mulde and Zwickauer Mulde and flows into the Elbe River north of

Dessau at river kilometer 307. At high water-levels the Mulde River is deemed to be the fastest flowing river in Central Europe. Due to its origin in a high-mineral and high-ore affected area it is the most significant reason for heavy metal input into the Elbe River and thus into the North Sea.

This research project was established to quantify the long-term effect of the former uranium mining and milling activities by investigating the uranium content of the water of the Mulde River. It is part of a work package dealing with transport and availability of uranium and its decay products in the Mulde floodplains, which in turn is part of a joint project on radionuclides in the environment and their transport to man via food chains, supported by the German Federal Ministry for Education and Research (BMBF).

Sampling and Analysis

A total of 26 water samples were collected in April, May and October 2008. 19 samples were collected along the course of the Zwickauer Mulde River and the Vereinigte Mulde River. Waters from the Freiberger Mulde River, the headwaters of the Zwickauer Mulde River, a small influent of the Zwickauer Mulde River, and from the Leine River near Hanover, respectively, were used as reference samples. Figure 1 shows the Mulde system and the sampling locations.

Generally, 4 L of water were collected at each sampling location. The water was filtered on-site using folded paper filters of a pore size of 7 µm. Subsequently, the samples were acidified with nitric acid to a pH of 1.5–2 and stored on ice in PE bottles.

In the laboratory the samples were filtered through cellulose nitrate filters of a pore size of 0.45 µm. The flowchart depicted in Fig. 2 gives an overview of the sample preparation steps. Uranium was concentrated by coprecipitation with ferric hydroxide and separated by solid-phase chromatography using UTEVA from Eichrom. For the coprecipitation procedure the samples were divided into aliquots of 1 L. 1 mL of ferric chloride solution (20 mg/mL) and 0.5 mL of U-232 tracer (~150 mBq/mL) were added to each aliquot. Then, 12 mL of concentrated ammonia solution were added after the solution had been heated up to a temperature close to the boiling point. The samples were then left to react overnight. After settling the supernatant was decanted, and the precipitates were washed three times with 10 mL of deionised water. During the washing procedure, the precipitates were remixed in pairs in order to reduce the number of aliquots per sample. After washing, the precipitates were dissolved in 10 mL hydrochloric acid (2 mol/L) and 2 drops concentrated hydrochloric acid. The samples were then purified in several steps: The first step, which was performed to separate lead and polonium from the sample, comprised solid-phase chromatography by Pb-resin (Eichrom), which was conditioned with 10 mL of hydrochloric acid (2 mol/L). The dissolved precipitate was eluted using 5 mL of hydrochloric acid (2 mol/L). The effluent was collected and concentrated to 1 mL. After adding 3 mL of concentrated nitric acid, the solution was evaporated to incipient dryness. In the second step the samples were taken up in 5 mL

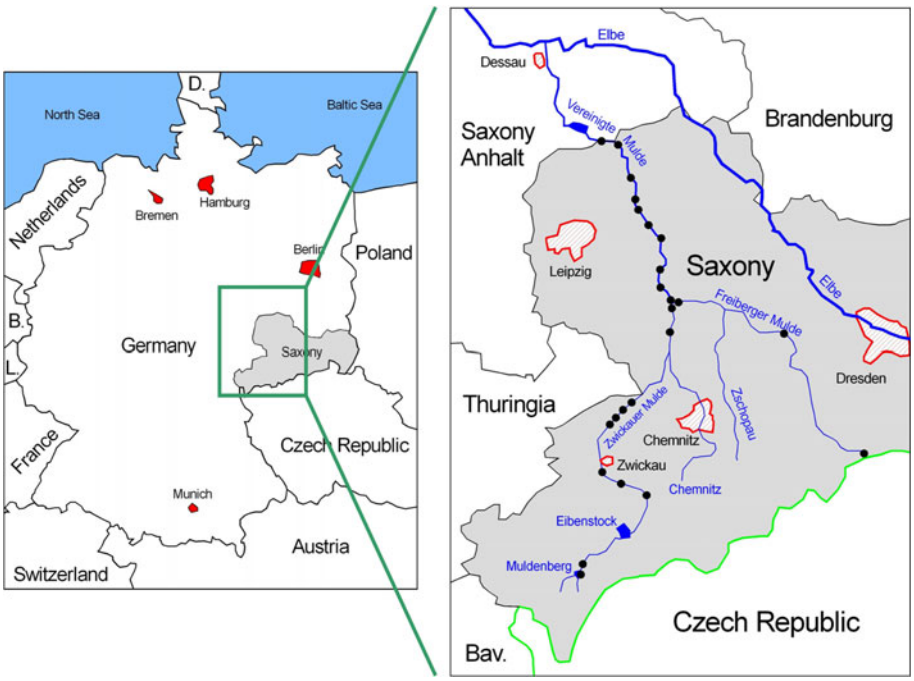

Fig. 1 The Mulde River system with the sampling locations

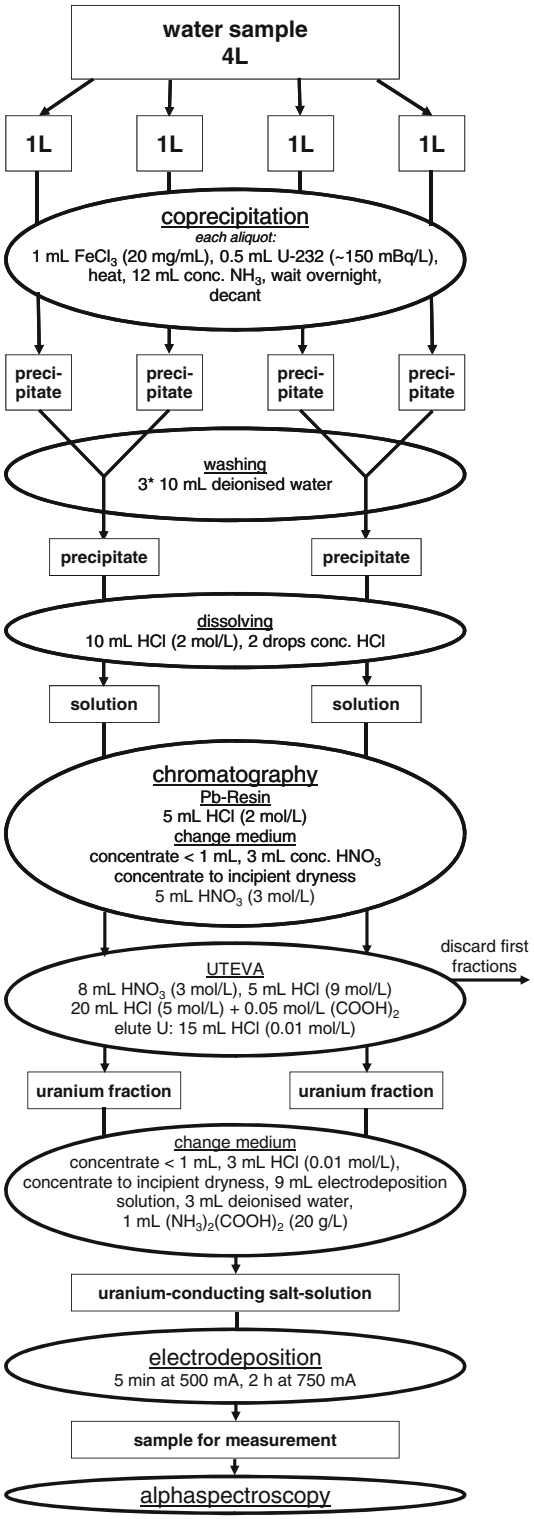

Fig. 2 Overview of the sample preparation steps

of nitric acid (3 mol/L), and passed through an UTEVA cartridge [1], which had been conditioned with 5 mL of nitric acid (3 mol/L). The cartridge was then rinsed with 8 mL of nitric acid (3 mol/L), 5 mL of hydrochloric acid (9 mol/L), and 20 mL of a solution containing hydrochloric acid (5 mol/L) and oxalic acid (0.05 mol/L). 15 mL of hydrochloric acid (0.01 mol/L) were added to the cartridge to elute the uranium. The aliquots were concentrated to a volume of 1–5 mL before being recombined to obtain the total sample. Again, the solution was evaporated to incipient dryness. The sample was suspended in a mixture of 9 mL of a special electrodeposition solution (composition: 2.5 mL 5 wt% $NaHSO_4$, 5 mL 15 wt% Na_2SO_4, 2 mL water), 3 mL of water, and 1 mL of ammonia oxalate (20 g/L). Following this procedure the sample was transferred to a stainless steel planchet via electrodeposition (5 min at 500 mA, then 2 h at 750 mA). Alpha-spectrometry was performed using a surface barrier detector.

The method was validated by the IAEA-2008-03 world wide open proficiency test on the determination of natural radionuclides in phosphogypsum and spiked water.

Results and Discussion

Table 1 summarises the measured activity concentrations of the uranium isotopes (U-238, U-234 and U-235). The samples are numbered consecutively in flow direction, in which the two letters denote the origin of the sample ("FM" = Freiberger Mulde River, "ZM" = Zwickauer Mulde River, "VM" = Vereinigte Mulde River). The Mulde River system has no official river kilometer system, thus, the dam of the Muldenberg reservoir (Gauss–Krüger coordinates: 4528788, 5586248) was defined as starting point. For the Freiberger Mulde River the headwaters (Gauss–Krüger coordinates: 5406939, 5619676) were defined as starting point. The uncertainties are given as combined A and B type standard uncertainty of measurement corresponding to GUM.

Additionally, values determined by Beuge et al. [2] between 1991 and 1993, i.e. directly after the abandonment, are presented for comparison in Table 2. The determination of the uranium concentration by Beuge et al. [2] was performed employing total-reflection X-ray fluorescence analysis (TXRFA). Measurements of samples collected along the Freiberger Mulde River and the Vereinigte Mulde River yielded values, which rarely exceeded the decision threshold of TXRFA at ~60 mBq/L (5 µg/L). Thus, they are not given here.

The measured values of the uranium isotopes (U-238, U-234 and U-235) exhibit the composition of natural uranium in almost all of the samples (see Table 1). This is in accordance with the expectation, as isotopic enrichment of uranium was no common practice in Germany.

The values can be divided roughly into three groups (see Table 1). The first group represents the reference values, which belong to non-affected areas with regard to uranium

Table 1 Activity concentrations (a) and related uncertainties [u (a)] for uranium in the water of the Mulde River; values denoted with "<" show the decision threshold (ISO 11929); sampling locations are specified by the corresponding river kilometers

		River kilometer (km)	U-238 (mBq/L)		U-234 (mBq/L)		U-235 (mBq/L)	
			a	u (a)	a	u (a)	a	u (a)
1	Leine	–	13.4	1.3	26.3	2.4	0.6	0.2
2	Bach	110	8.4	1.0	11.8	1.3	<0.7	–
3	FM1	5	2.6	0.3	2.7	0.3	0.2	0.1
4	FM2	67	2.0	0.2	2.2	0.3	<0.1	–
5	FM3	122	12.2	1.2	16.6	1.6	0.8	0.2
6	ZM1	−1	2.0	0.2	3.4	0.4	0.5	0.1
7	ZM2	5	3.0	0.4	3.5	0.5	<0.3	–
8	ZM3	53	73.9	7.5	74.0	7.5	2.0	0.7
9	ZM4	62	69.3	7.1	64.1	6.6	<1.9	–
10	ZM5	73	63.5	6.4	68.5	6.8	1.9	0.6
11	ZM6	102	79.0	6.8	84.2	7.2	2.9	0.4
12	ZM7	103	85.9	8.1	86.6	8.2	3.5	0.7
13	ZM8	108	83.7	7.7	95.2	8.6	4.4	0.7
14	ZM9	110	82.4	7.8	87.7	8.3	3.5	0.6
15	ZM10	151	69.5	5.8	80.0	6.7	4.9	0.4
16	ZM11	162	74.0	6.6	78.9	7.0	3.4	0.5
17	VM1	163	74.4	6.9	81.4	7.6	3.0	0.5
18	VM2	166	25.2	2.6	31.6	3.2	0.6	0.3
19	VM3	176	38.6	3.3	46.0	3.9	1.8	0.2
20	VM4	191	30.9	3.1	40.0	3.9	1.0	0.3
21	VM5	199	30.8	3.1	38.6	3.8	1.3	0.3
22	VM6	209	33.4	3.3	34.1	3.4	1.0	0.2
23	VM7	212	30.8	2.6	36.9	3.1	1.7	0.2
24	VM8	216	32.4	3.1	36.8	3.4	1.3	0.3
25	VM9	242	30.9	2.9	36.4	3.4	1.0	0.2
26	VM10	253	30.1	3.2	34.2	3.6	0.9	0.3

Table 2 Concentrations of uranium in the Zwickauer Mulde River determined by Beuge et al. [2]; sampling locations are specified by the corresponding river kilometers

Sampling location	River kilometer	β (U) (µg/L)	a (U-238) (mBq/L)
Weir Hartenstein	55	27	335
Short before Crossen	80	16	198
Near Glauchau	94	23	285
Near Sermuth	161	14	174

mining and milling activities. This includes the samples from the Freiberger Mulde River (FM1, FM2, FM3), from the small influent of the Zwickauer Mulde River (Bach), and the Leine River (Leine), as well as the samples ZM1 and ZM2 from the headwaters of the Zwickauer Mulde River. The mean activity concentration of U-238 for the reference samples is 6.2 mBq/L, which represents the background for unaffected surface water. Beuge et al. [2] determined a background value of 2.96 mBq/L in this area, which is in accordance with the results from our reference samples (FM1, FM2, ZM1 and ZM2). The average concentration of U-238 in surface waters in Germany lies in the range of 12.3–36.9 mBq/L (1–3 µg/L) [3], which is also reflected by the uranium concentration of the Leine River sample. The second group of values can be attributed to the Zwickauer Mulde River (ZM3 to VM1) with a mean value of 75.5 mBq/L for U-238. The third group consists of samples from the Vereinigte Mulde River (VM2 to VM10), showing a mean value of 31.5 mBq/L.

Figure 3 shows the variation of the activity concentrations of U-238 plotted against the river kilometers of the Zwickauer and Vereinigte Mulde River. The first two values were taken from the river source; they represent the natural background of uranium. About 4 km downriver of the dam of the Muldenberg reservoir and a few hundred meters downriver of the sampling location of ZM2, the river receives contaminated water from the mine Schneckenstein. The next sample (ZM3) was collected at Hartenstein, where the river has already passed the uranium mining area around Aue and Bad Schlema. Thus, the sample shows a high uranium activity. Following the course of the river to Zwickau (ZM5), the activity

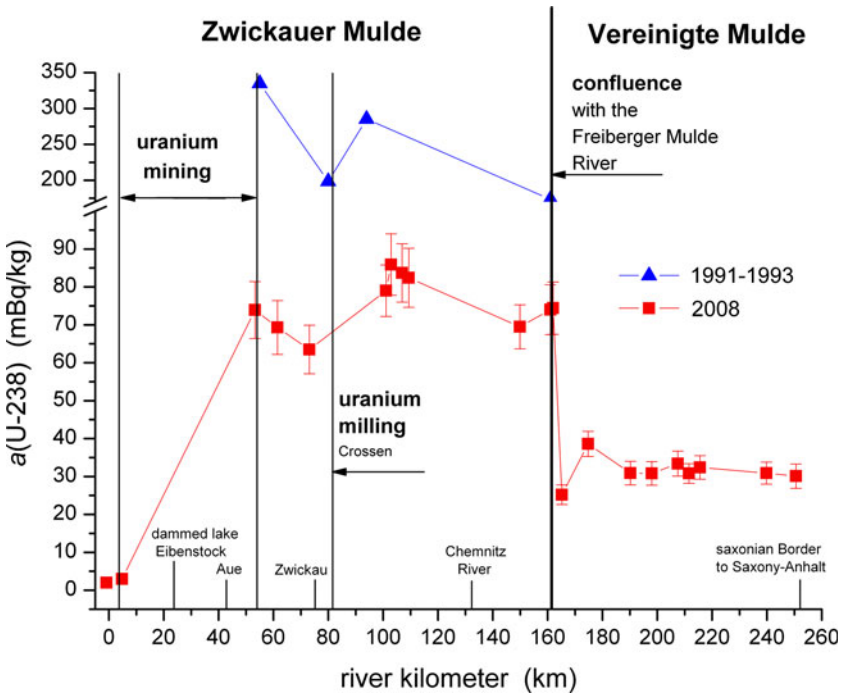

Fig. 3 Variation of the activity concentrations of U-238 in water of the Mulde River, plotted against the river kilometers; comparative values for the years 1991–1993 adapted from Beuge et al. [2]

concentrations seem to decrease slightly. This effect can be explained by dilution with less contaminated water from tributaries. Downstream of Zwickau the activity concentration of uranium in the water increases again. This increase results from the effluents of the former uranium milling industry site near Crossen. In the further course of the Zwickauer Mulde River, the activity remains approximately constant until the confluence with the Freiberger Mulde River. Due to measurement uncertainties, the values are in agreement with a slight, but not significant decrease of the activity concentration corresponding to dilution caused by tributaries, especially by the Chemnitz River, which is the largest tributary of the Zwickauer Mulde River. In contrast, a considerable decrease in the activity concentration of uranium, which is significant, occurs downriver of the confluence of the Zwickauer Mulde River with the uncontaminated Freiberger Mulde River due to the stronger dilution effect.

The measurements from the early 1990s [2] show the same characteristics, but at a much higher activity level. During the last 20 years, the contamination of the Mulde River decreased considerably, on average by a factor of 3.4. This effect results from the decreasing emission due to the remediation activities in this area, the most important of which are the water treatment facilities erected to purify the effluents from the former uranium mining and milling facilities, e.g. tailing ponds and mining dumps.

The activity concentration of uranium remains constant along the Vereingte Mulde River, showing an arithmetic mean of 31.5 mBq/L. The variation of the first three measured values only reflects inhomogeneous and slow mixing of waters of the two rivers, as the samples were taken at different sides of the Vereinigte Mulde River. No decrease of the uranium activity along the Vereinigte Mulde River can be observed, since the dilution by smaller tributaries along the river here is negligible.

Radiological relevance

The uranium concentrations found in river water are insignificant from the radiological point of view. The recommended value for uranium in drinking water based on its toxicity given by the Federal Environment Agency (UBA) is <10 µg/L [4]. This corresponds to an activity concentration of U-238 of 123.5 mBq/L. In none of the samples the uranium activity exceeds this value.

Conclusions

During the last 20 years, the contamination of the Mulde River decreased by at least a factor of three. This effect mainly results from the decreasing emission due to the remediation activities. On the other hand, an influence of the former uranium mining and milling activities can still be detected. The activity concentration of uranium in samples from the Zwickauer Mulde River is still high compared with the natural background. The values measured in the water of the Vereinigte Mulde River are also elevated, but to a lesser extent due to the dilution effect caused by the merging with the non-affected Freiberger Mulde River.

Acknowledgment This research project is supported by the German Federal Ministry for Education and Research (BMBF).

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