Uranium contents in acidic lakes and groundwater of Lower Lusatia (Germany)

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Abstract. Acidic pit lakes are typical for the landscape of Lower Lusatia. The lakes of a former lignite mine were investigated to find remediation strategies. Hydrogeology and geochemistry of the drainage basin were characterized by collecting numerous data. This study is focussed on the geochemistry of uranium. The investigated waters have low U concentrations (≤ 2 µg/l). There is no definite correlation between pH and U concentration.

Introduction

There are more than 100 acidic pit lakes in Lower Lusatia (Germany) caused by pyrite oxidation in the surrounding dump sediments (Geller et al. 1998). A sequence of such pit lakes developed in the former lignite mine Plessa-Koyne.

The pH-values of these lakes lie between 2.4 and 3.0. Therefore, the biological diversity is limited due to the unfavourable living conditions. The lakes can be used neither as a drinking water reservoir nor as recreation sites. The geochemistry including the uranium contents of three acidic pit lakes ("RL 107", "RL 111", "RL 117") was investigated (Fig. 1). Mining periods and morphological data of the investigated lakes are given in Table 1.

Table 1. Description of the investigated pit lakes (LENAB 1998).

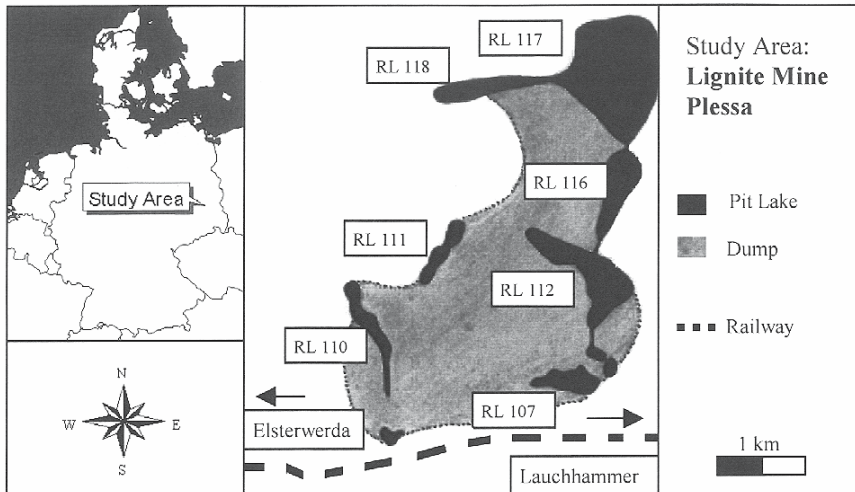|	RL 107	RL 111	RL 117
Mining period	1897 - 1928	1929 - 1958	1956 -1966
Water level (m a.m.s.l.)	92.3	94.1	92.3
Area (m^2)	122,000	107,000	950,000
Max. depth (m)	4.0	10.2	14.0
Average depth (m)	1.9	4.6	11.0

Fig. 1.   The former lignite mine with the acidic pit lakes (Bozau and Strauch 2002).

Methods

The geochemistry including U and Th contents of three acidic pit lakes, as well as in pore water of the lake sediments, surrounding groundwater and dump sediments of the lake "RL 111" were investigated.

Lake water of several depths was taken by a water sampler. Groundwater was sampled by pumping, sediments by digging and drilling. The sediments were digested with acid (HNO_3/HCl) by microwave extraction to analyse trace elements, and also used for leaching experiments according to DIN 38414/4 (water-extractable contents). Chemical analyses were performed by ionic chromatography (SO_4^{2-}, NO_3^-, Cl^-), photometry (NH_4^+), and ICP-OES (Ca, Mg, K, Na, Fe_{tot}, Al) on 0.2 µm filtered water samples.

U and Th analysis was carried out on the 0.2 µm filtered and acidified water samples, as well as the sediment digests by ICP-MS using a Perkin Elmer ELAN 5000a instrument. The detection limit was 0.007 µg/l. The isotopes chosen for the measurement were ^{238}U and ^{232}Th.

Results and discussion

The lake water of all investigated lakes has low pH-values (≤ 3.0) as well as high iron and sulphate concentrations (Table 2). Lake "RL 107" has the lowest pH (2.4) and the highest iron and sulphate concentrations, whereas the lake "RL 117" with a pH-value of 3.0 shows lower iron and sulphate concentrations. These differences can be explained by the amount of inflowing acidic groundwater, which is correlated to the extent of the bordering dump area. Erosion processes from the dump sediments on the lake shore also contribute to the lake acidification.

K, Na, and Cl are not increasing with lower pH-values. The lowest values of these elements are found in pit lake "RL 107". It is possible that the precipitation of minerals from the lake water is responsible for this. K and Na are precipitating within jarosite $[(H,K,Na)Fe_3(OH)_6(SO_4)_2]$ as investigated in the lake "RL 111" (Göttlicher et al. 2001). U concentrations of the lake water lie between 0.04 and 2.1 µg/l (Fig. 2). WHO guidelines for drinking water give a provisional limit of 2 µg U/l (Reimann and Banks 2004).

The highest U concentration is found in the lake "RL 111". The differences within the water column of lake "RL 111" can be explained by an increased groundwater inflow to the deepest part of the lake (Knöller 2000). The chemical differences within the water column of the lake "RL 107" are caused by the melting of the ice cover. The ice cover prevents the wind from mixing the water column, while its melting leads to lower concentrations in the upper water layer. After the mixing of the whole water column in spring, no chemical differences will occur. The shallow depth (max. 4 m) and the meteorological conditions do not allow a stable stratification of the lake "RL 107" (Schimmele 2000). Due to its wide

Table 2. Chemical characteristics of the lakes (SHE = Standard Hydrogen Electrode).

	RL 107 March 2003		RL 111 August 2003		RL 117 June 2003	
Water depth	0 m	4 m	0 m	10 m	0 m	12 m
pH	2.6	2.5	2.6	2.8	3.0	2.8
Eh (mV, SHE)	770	680	760	590	670	690
Cond. (mS/cm)	1.6	3.0	2.6	1.8	0.9	0.9
Ca (mg/l)	151	356	196	254	85	74
K	0.9	1.7	2.7	5.8	4.2	3.6
Mg	18	44	25	32	13	11
Na	3.0	6.4	5.9	8.0	8.3	7.8
SO_4 (mg/l)	1360	3260	1220	1700	387	385
Cl	6.0	10	8.3	8.1	13	13
Fe (mg/l)	265	730	134	341	10	10
Al	29	64	33	36	1.2	1.0
DOC (mg/l)	2.3	4.5	0.5	5.7	0.5	0.5
U (µg/l)	0.6	1.0	2.1	1.1	0.05	0.04
Th	0.5	0.7	1.3	0.6	0.08	0.07

surface and wind stress, lake "RL 117" is relatively well mixed during all seasons. Therefore, no significant chemical differences within the water column can be measured. Speciation calculations for the lake waters were performed using the code PHREEQC (Parkhurst and Appelo 1999). According to Gammons et al. (2003), the sulfate complexes UO_2SO_4 and $UO_2(SO_4)_2^{2-}$, as well as UO_2^{2+} are dominant in all waters.

The groundwater of the drainage basin of lake "RL 111" is characterised by lower concentrations (0.01-0.6 µg/l) than the lake, whereas the water-soluble fraction of dump sediments shows maximum uranium concentrations up to 50 µg/l (Fig. 3).

Uranium concentrations from 3 to 6 mg/kg in lignite (4 samples from boreholes near lake "RL 111") and from 2 to 4 mg/kg in dump sediment (3 samples of the shore of lake "RL 111") were analysed. These concentrations are slightly higher than the U contents of the upper crust (0.91 mg/kg, Taylor and McLennan 1985; 1.8 mg/kg, Mason and Moore 1985).

There is a good correlation between the pH-value, the sulphate and iron concentrations in the water of the three investigated lakes. But the uranium contents
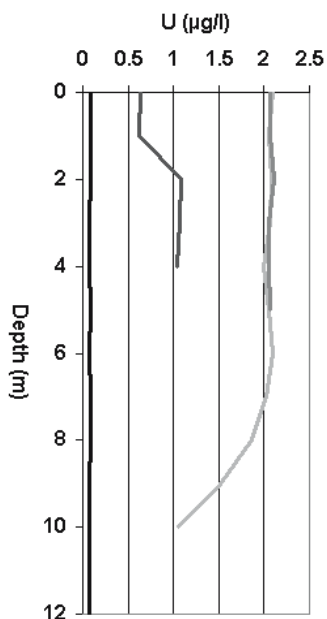

Fig. 2.   U in the water column of the investigated lakes RL 107 – March 2003 (after melting of the ice cover), middle of the lake (4 m) RL 111 – August 2003, north (6 m) and middle basin (10 m) RL 117 – June 2003, middle of the lake (12 m).

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of the lake water do not really correlate with the pH-values (Fig. 3 and Table 2). The anoxic groundwater has lower contents than the water of the lakes "RL 107" and "RL 111".

The conventional geochemical behaviour that Fe(II) of anoxic water is more soluble and the oxidized Fe(III) tends to precipitate, whereas U(IV) is almost insoluble and the oxidized U(VI) is well soluble (e.g. Kronfeld et al. 2004) cannot be easily applied to the drainage basin of the acidic lake "RL 111".

According to the mixing model of lake "RL 111" (Fig. 4; Bozau et al. 2004), chloride can be considered as a conservative tracer. Iron precipitates during the groundwater inflow to the lake. The water mixing model of lake "RL 111" does not explain the uranium distribution. There is more U in the lake than in the inflowing groundwater. One possible explanation might be that during the groundwater inflow into the lake sediments, geochemical changes (e.g. oxidation of Fe(II) to Fe(III), precipitation of hydrous ferric oxides and the pH-decrease) lead to a release of uranium. But pore water profiles of lake "RL 111" indicate that higher U concentrations in the pore waters are correlated to the higher contents of Fe minerals (as goethite and jarosite) in the sediments (data not shown). These different observations for the lake water, the pore water of the lake sediments and the inflowing groundwater at the same lake are in contrast.

It could be that the weathered sediments dumped on the lake shores and reaching the lake water by erosion processes are also an important source of uranium (Fig. 3). Gammons et al. (2003) also consider this hypothesis for their investigated lake: "An alternative hypothesis is that UO_2^{2+} behaves conservatively, and that its concentration is simply a function of the rate of input from weathering and wall-rock leaching compared to the total water flux."
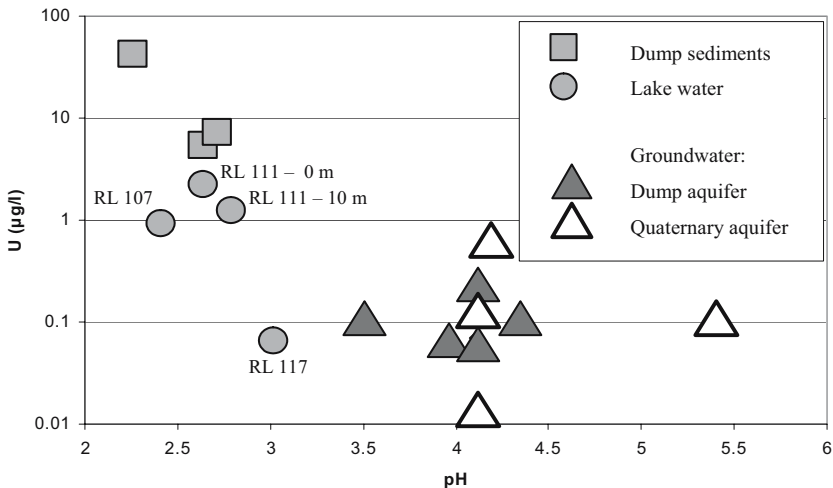

Fig. 3.   U concentration against pH-value (Lakes "RL 107", "RL 111" "RL 117", groundwater and leached dump sediments).

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The Th concentrations of lake "RL 107" and "RL 111" are lower than the U concentrations, whereas lake "RL 117" shows an opposite concentration ratio (Table 2). The data measured for Th indicate the same geochemical behaviour as already discussed for U. In the drainage basin of the lake "RL 111" groundwater has Th concentration from 0.01 to 0.1 µg/l. The surface water of the lake shows Th concentrations of 1.3 µg/l. According to the higher groundwater inflow (with lower Th concentrations) to the deepest part of the lake, a Th concentration of 0.6 µg/l was analysed for the water sampled at 10 m.

Fe

| 64 | 145 | 828 |

Quaternary aquifer   Dump aquifer

U (µα/l)

| 0.1 | 2 | 0.1 |

Quaternary aquifer   Dump aquifer

Cl

| 15 | 16 | 22 |

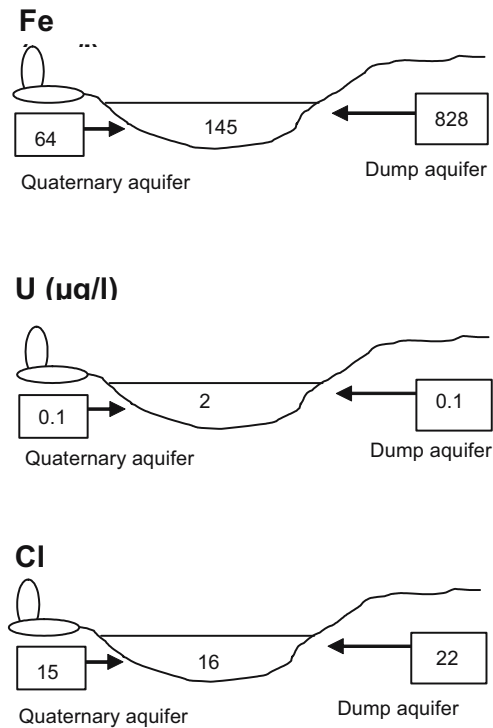Quaternary aquifer   Dump aquifer

Fig. 4.   Interaction of lake and groundwater as a mixing model of lake "RL 111". The lake water concentration can be analysed (data shown above) or calculated according to the amount of inflowing groundwater (Bozau et al. 2004). The differences between the analysed and calculated concentrations lead to conclusions about the geochemical behaviour of the elements. Behaviour of Fe (precipitation of hydrous ferric oxides, analysed < calculated concentration), Cl (non reactive tracer, analysed = calculated con-centration) and U (unknown source, analysed > calculated concentration).

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Conclusions

Compared to acidic waters which resulted from ore mining (Elbaz-Poulichet et al. 1999, Gammons et al. 2003), or neutral waters from bedrock wells in granitic/gneissic formations (Frengstad et al. 2000), the U concentrations of the investigated acidic pit lakes are low.

To explain the higher U and Th concentrations in the lake "RL 111" compared to the inflowing groundwater, further investigations considering erosion processes and particle transport are necessary. According to the investigation of Reiller et al. (2002), the interaction between U, Th and natural organic matter (escpecially the complexation with humic/fulvic acids, as well as their sorption on hydrous ferric oxides) in acidic waters should be involved in these investigations.

Furthermore, the geochemical behavior of U and Th is quite different from the geochemistry of rare earth elements (REE) studied in the drainage basin of lake "RL 111" by Bozau et al. (2003 and 2004). The REE concentrations and patterns allow the distinction between the two aquifers filling that lake, whereas U does not follow this trend. Therefore, results of REE studies of acidic waters should not be simply transmitted to the behavior of actinides.

Acknowledgements

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