TRLFS study on the speciation of uranium in seepage water and pore water of heavy metal contaminated soil

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Abstract In situ leaching of uranium ores with sulfuric acid during active uranium mining activity on the Gessenheap has caused longstanding environmental problems of acid mine drainage and elevated concentrations of uranium. To study there remediation measures the test site Gessenwiese, a recultivated former uranium mining heap near Ronnenburg-East Thuringia/Germany, was installed as a part of a research program of the Friedrich-Schiller University Jena to study, among other techniques, the phytoremediation capacity of native and selected plants towards uranium. In the first step the uranium speciation in surface seepage and soil pore waters from Gessenwiese, ranging in pH from 3.2 to 4.0, were studied by time-resolved laser-induced fluorescence spectroscopy (TRLFS). Both types of water samples showed mono-exponential luminescence decay, indicating the presence of only one major species. The detected emission bands were found at 477.5, 491.8, 513.0, 537.2, 562.3, and 590.7 nm in case of the surface water samples, and were found at 477.2, 493.2, 513.8, 537.0, 562.4, and 590.0 nm in case of the soil water samples. These characteristic peak maxima together with the observed mono-exponential decay indicated that the uranium speciation in the seepage and soil pore waters is dominated by the uranium (VI) sulfate species UO$_2$SO$_4$(aq).

Due to the presence of luminescence quenchers in the natural water samples the measured luminescence lifetimes of the UO$_2$SO$_4$(aq) species of 1.0–2.6 µs were reduced in comparison to pure uranium sulfate solutions, which show a luminescence lifetime of 4.7 µs. These results convincingly show that in the pH range of 3.2–4.0 TRLFS is a suitable and very useful technique to study the uranium speciation in naturally occurring water samples.

Keywords Time-resolved laser-induced fluorescence spectroscopy · TRLFS · Uranium (VI) · Speciation · Pore water · Seepage water

Introduction

Phytoremediation is considered a clean, cost-effective and non-environmentally disruptive technology and relies on the ability that plants take up nutrients and toxic heavy metals from the surrounding pore water. This technique has been successfully applied in experiments concerning the restoration of abandoned metal-mine workings [1]. In case of increased uranium concentrations in the pore water, uranium may enter the plants, which grow on the contaminated site and accumulate in certain plant compartments, e.g., leaves and stems. Recent studies have shown that different plants species incorporate different amounts of uranium. This fact is decisive in selecting plants as hyperaccumulators to bioaccumulate uranium for remediation purposes of heavy metal contaminated soils by bio/phytoremediation.

As part of a research program of the Friedrich-Schiller University Jena for investigations of acid mining drainage (AMD) and heavy metals retention, especially uranium [2], as well as heavy metal uptake and accumulation into
plants, test site Gessenwiese, a recultivated former uranium mining heap close to Ronneburg in Eastern Thuringia was installed. AMD is a severe environmental problem characterized by very metal-rich waters, high sulfate concentrations and low pH. In combination with uranium mining AMD at the Gessenwiese was generated by in situ leaching of uranium ores with sulfuric acid. Despite the high concentrations of toxic heavy metals in the Gessenbach heap drainage waters many microorganisms thrive in this low pH environment and have been identified by [3, 4].

The aim of this study was to identify the speciation of aqueous uranium in surface and pore water, surrounding the plant roots growing on the test site Gessenwiese by time-resolved laser-induced fluorescence spectroscopy (TRLFS). TRLFS combines very low detection limits and a high sensitivity toward U(VI) complex formation in aqueous solutions [5, 6] and was used to identify the uranium speciation of sorbed uranium on different mineral surfaces [7–9], in solutions prepared in the laboratory [10], in thin mineral coatings [11, 12], and in waters from AMD [13]. Uranium has various oxidation states (i.e., III–VI) and it is well established that its transport behavior strongly depends on its oxidation state [13]. In contrast to tetravalent uranium, U(VI) is much more soluble and may migrate in the environment in dissolved form via the water path. Geochemical predictions indicate that the dissolved metals in the acid mine waters are likely present in the form of either individual free ions or as some different sulfate ionic species [14]. Sulfate is able to form strong complexes with uranium and thereby strongly affects its speciation and migration [15]. Uranium sulfate complexation has been studied by TRLFS and X-ray absorption spectroscopy (EXAFS) for simple two component solutions prepared in the laboratory [15–18] and thermodynamic data are available for three sulfato species, UO₂SO₄(aq), UO₂(SO₄)²⁻, and UO₂(SO₄)⁴⁻ [16, 19, 20].

The speciation of uranium in the complex pore water solution, i.e., real solution and not a synthetically prepared two component solution, surrounding the plant roots was investigated and should be the basis for a comparison with the present uranium speciation in certain plant compartments. From a comparison of the identified speciation outside and inside of the plant in the respective plant compartment conclusions should be drawn about how the uranium speciation changes during the transport into the plant and how the plant barrier were passed. This study should contribute to better understand the mechanisms of how uranium enters plant cells and how this knowledge can be applied to extract more uranium from contaminated soils by phytoremediation.

**Experimental**

**Sampling campaign**

The surface water samples OW1 and OW2 were collected in and close to the test site Gessenwiese (see Fig. 1) from a

![Fig. 1 Test site Gessenwiese in eastern Thuringia (left), and sample localities within test site. Coordinates are in the German grid (Gauß-Krüger zone 4)](image-url)
little creek in the north of the test site on the 29th of March in 2009. Soil water samples (BW1–BW3) were taken from the site section MF 3 (Fig. 2) on the 19th of November 2009. The test field “Gessenwiese” is on the ground of a former leaching heap, a legacy of the uranium mining activity, close to Ronneburg and located between the villages Kauern and Grobsdorf (eastern Thuringia). The top of leaching heap was removed and replace by approximately one meter thick soil cover. A more detailed description of the history and composition of the Gessenwiese are found by [2].

Water analyses

All water samples investigated in this study show a low pH, and contain high concentration in heavy metals, including uranium, and a high concentration in sulfate. These results are in agreement with data published in [21].

The chemical composition of seepage water samples (OW1 and OW2) and soil water samples (BW1–BW3) were analyzed for cations by inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS) for Na, K, Mg, and Ca, and graphite furnace atomic absorption spectrometry (GFAAS) for Fe, respectively. An ELAN 9000 type ICP-MS spectrometer (Perkin Elmer SCIEX, Waltham, Massachusetts, USA), a Perkin Elmer 4100 AAS, and an AAS-6F ZEEnit 600s Graphite furnace AAS with Zeeman background correction (Analytik Jena, Jena, Germany) were used for these analyses. The error of the chemical analysis for AAS analyses is only 1–2 and 5–10% for ICP-MS measurements. Anions, i.e., chloride, nitrate, phosphate and sulfate were determined by ion chromatography (IC-system 732/733, Metr-ohm, Filderstadt, Germany). The analytical error for the anion analyses is smaller than 5%. Total organic carbon (TOC) and total nitrogen (TNb) were obtained by a Multi-N/C 2100 (Analytik Jena, Jena, Germany). The concentrations of selected anions from the two investigated surface water samples and the three soil water samples, together with the measured pH values are listed in Table 1. Metal concentrations from these sampling sites are shown in Table 2.

Table 1 Concentrations of anions, total organic carbon (TOC), and total nitrogen (TNb) in mg/L; and pH of the water samples. Uncertainty values are between 3 and 10%

|                | OW1 | OW2 | BW1 | BW2 | BW3 |
|----------------|-----|-----|-----|-----|-----|
| Chloride       | 48.8| 82.6| 3.75| 1.85| 11.4|
| Nitrate        | <2  | <2  | <2  | <2  | <2  |
| Phosphate      | <5  | <5  | <5  | <5  | <5  |
| Sulfate        | 3520| 4480| 966 | 1010| 2530|
| TOC            | 7.54| 4.90| 6.38| 2.36| 2.04|
| TNb            | 0.50| 0.46| <0.2| 0.60| 0.25|
| PH             | 3.84| 3.76| 4.02| 3.40| 3.27|

Description of the TRLFS analyses

Time-resolved laser-induced fluorescence spectroscopy (TRLFS) possesses some superior features, above all a very high sensitivity for fluorescent heavy metal ions. The superiority of TRLFS compared to other spectroscopic techniques, e.g., was showed in [12].

The measurements were made with the untreated samples, directly after they were filled in quartz glass cuvettes. Within the few days between taking samples and TRLFS measurements the samples were stored at 2 °C in the refrigerator. TRLFS measurements of all water samples presented here were carried out at room temperature. The TRLFS system consists of a Nd:YAG diode laser (Inlite Continuum), where the actual laser power was monitored with an optical power meter (model LabMaster, Ultima Coherent, USA) to allow for corrections due to fluctuations in the laser power. The excitation wavelength was 266 nm. The resulting generated luminescence signal was collected perpendicular to the excitation beam and focused into a fibre optic cable that was coupled to the slit of a triple-grating spectrograph (0.5 m spectrograph, model 1236 OMA, Princeton Applied Research, USA). The luminescence spectra were measured by a charge-coupled device.
(CCD) camera (model 7467-0008, Princeton Instruments, Inc., USA), which was cooled to 18 °C.

The spectra were recorded in the wavelength range from 430 to 600 nm. Exposure time from the camera was set to 2 μs. In steps of 100 ns, the delay time for each following exposure after the excitation laser pulse was recorded and ranged from 30 to 8 030 ns. The average laser power was approximately 3 mJ. For every delay time, every luminescence spectrum was measured three times, and for each spectrum 100 laser shots were averaged. All functions (time controlling, device settings, recording of the spectra, data storage) of the spectrometer were computer controlled.

The computer software WinSpec/32 version 2.5.19.0 (2000–2003 Roper Scientific VBScript, Microsoft Corp) was used for the deconvolution of the spectra. The decay equations and life time curves of the spectra were calculated with the Origin 7.5G (OriginLab Corporation, Northampton, MA, USA) program. Another more detailed data processing procedure, described in [12] was used in the data evaluation process too, and both methods delivered similar numerical results. The acquired TRLFS spectra displayed a high signal-to-noise ratio and sharp emission bands.

## Results

TRLFS results on the uranium speciation were obtained for natural surface and soil water samples collected from the Gessenwiese test site. These samples represent complex natural solutions containing a multitude of components. They were no simple two component samples synthesized in the laboratory.

Generally, TRLFS provides two kind of spectroscopic information: the position of the emission maxima and the luminescence lifetime. In a fingerprinting procedure the measured TRLFS spectra are then identified with the help of previously recorded reference substances. At an excitation wavelength of 266 nm, the luminescence quantum yield for uranium (VI) is very high, and the respective uranium (VI) luminescence is detected in the range 470–600 nm [22].

### Surface water samples

Both samples delivered an evaluable luminescence signal for TRLFS which were characteristic for uranium luminescence. A time-resolved luminescence spectrum of sample OW2 is shown in Fig. 2 and the respective emission bands are summarized in Table 3. The TRLFS-signals of both water samples showed a mono-exponential decay, indicating the presence of only one main species. The observed emission bands of these samples were found at 477, 491, 513, 537, 562, and 591 nm (478–492–513–538–562–590). The positions of the six recorded peak maxima for both water samples were in agreement with data for reported uranium sulfate species [13, 16, 18, 23]. The intensity of the luminescence signal from sample OW1 is about half of the intensity of sample OW2 and is characteristic for the different uranium content of these samples [75.1 and 291 μg/L, respectively] (Table 2). The characteristic positions of peak maxima together with the

| Metals  | OW1 | OW2 | BW1 | BW2 | BW3 |
|---------|-----|-----|-----|-----|-----|
| Na      | 7040 | 8570 | 1920 | 1540 | 2520 |
| Mg      | 622000 | 849000 | 52500 | 11000 | 133000 |
| Al      | 30100 | 43100 | 21500 | 31700 | 100000 |
| Si      | 18600 | 22300 | 28900 | 32800 | 49500 |
| K       | 4890 | 5350 | 830 | 1240 | 2100 |
| Ca      | 344000 | 340000 | 209000 | 244000 | 389000 |
| Mn      | 86600 | 97400 | 12000 | 1870 | 23700 |
| Fe      | 8070 | 5390 | 2420 | 15500 | 18300 |
| Co      | 2050 | 2910 | 331 | 102 | 1000 |
| Ni      | 11400 | 14200 | 1920 | 751 | 6370 |
| Cu      | 54.3 | 293 | 1120 | 1490 | 3600 |
| Zn      | 1760 | 2870 | 1130 | 1490 | 2840 |
| As      | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Sr      | 518 | 612 | 136 | 81.2 | 251 |
| Cd      | 14.1 | 43.3 | 24.4 | 9.76 | 107 |
| Ba      | 17.2 | 16.1 | 10.6 | 7.02 | 7.36 |
| Pb      | 64.4 | 31.1 | 1.87 | 0.508 | 8.63 |
| U       | 75.1 | 291 | 322 | 156 | 890 |
observed mono-exponential decay revealed without doubt that the uranium speciation in the seepage water is dominated by the uranium (VI) sulfate species UO$_2$SO$_4$(aq). A respective mono-exponential decay curve from sample OW1 is shown in Fig. 3.

Speciation calculations, however, predict also the presence of UO$_2$$^2$? ("free uranyl") and the UO$_2$(SO$_4$)$_2$$^-$ species as minor components. These calculations were made with the geochemical speciation code EQ3/6 [24] and the software "Geochemists Workbench" Version 8.0.8/ACT2 [25], using formation constants of NEA report [20], and using the respective surface water compositions of the sample sites. In contrast to the obtained results obtained for the speciation calculations, no spectroscopic evidence for any additional uranium species was found by TRLFS.

However, the observed lifetimes of the two uranium luminescence signals were 1.6 and 1.0 µs, respectively, and thus (Table 3) shorter than reported lifetime for uranium sulfate species found in literature of 4.3 and 4.7 µs [13, 17]. These shortened lifetimes of the uranium sulfate luminescence signal from the investigated natural samples was attributed to the presence of luminescence quenchers in the samples, e. g., iron, manganese, and organic substances. The different lifetimes of the luminescence signals in the two surface water samples investigated here were explained with the different concentrations of potential quenchers in the two samples.

Pore water samples

All three pore water samples from the test field showed also an evaluable luminescence signal for TRLFS with mono-exponential luminescence decay. The reproducibility of the positions from the peak maxima from the luminescence spectra within the three soil water samples BW1, BW2, and BW3 is satisfactory. The means of the positions of the peak maxima of 477.2, 491.5, 513.3, 536.8, 562.1, 591.3 µs, compared with data published in [18] and [13]

| Peaks | OW1 | OW2 | Means (surface wtrs.) | [18] | [13] |
|-------|-----|-----|-----------------------|-----|-----|
| OW1   |     |     |                       |     |     |
| OW2   |     |     |                       |     |     |
| Means (surface wtrs.) | 477.5 | 491.8 | 513.0 | 537.2 | 562.3 | 590.7 |

Table 3  Positions of the peak maxima of the luminescence signals OW1 and OW2 in nm and their means in nm, rounded to one decimal place (uncertainty values are ±0.3 nm), and lifetime of the signals $t$ in µs, compared with data published in [18] and [13]

![Fig. 3 Life time curve from the luminescence signal sample OW2](image1)

![Fig. 4 Intensity from the luminescence signals of the three pore water samples, in comparison with positions of peak maxima published in [13] for UO$_2$SO$_4$(aq) (dashed vertical lines)](image2)
for the first spectrum (Fig. 4). These results obtained for the pore water samples were summarized in respect to positions of the peak maxima and their respective lifetimes of the signals Table 4.

As in the analyzed surface water samples from the test site Gessenwiese show the pore water samples from the Gessenwiese characteristic positions of the peak maxima and a mono-exponential decay. By comparing these spectra with spectra obtained for uranyl sulfate reference substance it was found that the uranium speciation in the soil water samples is dominated by the uranium (VI) sulfate species UO_2SO_4(aq), no evidence for the presence of the so called “free uranyl” was found in this samples by TRLFS. But it could be, that a possible signal from free uranyl was suppressed by the intensive signal from the UO_2SO_4(aq) species. However, also the mono-exponential decay curves indicate only one species. Same as in case of surface water samples, no hint was found for additional uranium species by TRLFS in these soil water samples. This was in contradiction to results of speciation calculations based on soil water compositions of three different data sets.

The different lifetimes of the luminescence signals in the three soil water samples, ranging from 1.0 to 2.6 μs, were again related to the presence of luminescence quenchers in different concentration ratios. In case of the soil water samples there seems to be a dependency between life time of the uranium luminescence signal and iron concentration in the sample: The higher the Fe concentration in the soil water sample, the shorter becomes the uranium luminescence signal (Tables 2 and 4).

**Conclusion**

So it was showed that TRFLS can be a useful tool for clearing up the speciation of uranium in water, which is affiliated by plants.

Uranium speciation in two natural occurring seepage water samples, OW1 and OW2, and three soil water samples, BW1, –2, and –3, all samples from test site Gessenwiese, were analyzed by TRFLS. All five samples delivered an evaluable luminescence signal for TRFLS. The positions of the six peak maxima from these five water samples were very well in agreement with already published information on synthetically prepared uranyl sulfate solution [17, 18] and with data obtained from an uranium containing acid mine drainage environment [13]. The TRFLS-signals of all five water samples show in addition a mono-exponential decay, indicating the presence of one major uranium species. These two characteristics, i.e., positions of peak maxima and the observed mono-exponential decay of the luminescence signal revealed that the uranium speciation in the surface water and the pore water samples is dominated by the uranium (VI) sulfate species UO_2SO_4(aq). Except for this uranium species UO_2SO_4(aq) no hint for a second or a third uranium species was found by TRFLS, in contrast to results obtained by speciation. The luminescence life time of this UO_2SO_4(aq) species decreases in the presence of luminescence quenchers, in particular iron ions. The higher the iron concentration, the shorter becomes the uranium luminescence life time. This is one strong piece of evidence that iron plays an important role in quenching the uranium (VI) luminescence signal lifetime in natural occurring water samples.

The TRFLS analyses were performed to identify the uranium speciation in the surface water and pore water surrounding plant (plant roots). In a later stage these results will be compared with the uranium speciation identified in plants and plant compartments, respectively, which grow on the test site Gessenwiese within a phytoremediation study. These plants take up the same uranium contaminated water during their growth, in which the uranyl sulfate species UO_2SO_4(aq) dominates.

It was showed that TRFLS is a suitable tool for identifying the speciation of uranium in complex natural waters, which contain a multitude of different ions and complexes.

TRLFS measurements with the aim to identify the uranium speciation in different plant compartments (e.g., roots, leaves, shoots) which grow in association with the pore water will be carried out in future TRFLS investigations. The results will then be compared with identified uranium speciation in surface and soil water of the

Table 4 Positions of the peak maxima from the luminescence signals of three pore water samples and their means in nm, rounded to one decimal place (uncertainty values are ±0.3 nm), compared with data published in the literature [13, 18], and lifetime of the signals $t$ in μs.

|        | First peak | Second peak | Third peak | Fourth peak | Fifth peak | Sixth peak | $t$ |
|--------|------------|-------------|------------|-------------|------------|------------|-----|
| BW1    | –          | 492.2       | 513.7      | 537.3       | 562.5      | 590.2      | 2.6 |
| BW2    | –          | 492.3       | 513.2      | 535.3       | 562.5      | –          | 1.7 |
| BW3    | 477.2      | 493.2       | 514.5      | 538.5       | 562.3      | 589.7      | 1.0 |
| Means (pore waters) | 477.2 | 492.6 | 513.8 | 537.0 | 562.4 | 590.0 |       |
| [18]   | 477        | 493         | 515        | 538         | 565        | –          | –   |
| [13]   | 477.5      | 492.8       | 514.1      | 537.5       | 563.0      | 590.1      | 4.7 |
Gessenheap in order to better understand the uranyl transport in cell and to better assess the phytoremediation ability of certain plants. Plant samples of different plant compartments useful for TRLFS investigations can be obtained by centrifugation as cell sap, or as solid milled plant compartment sample [26]. The reactivity and toxicity of uranium depend on the speciation of heavy metals and thus has to be considered as important possible risk factor as uranium may enter economic plants and eventually arrives in the food chain.

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