



Uranium concentrations in sediment pore waters of Lake Neusiedl, Austria

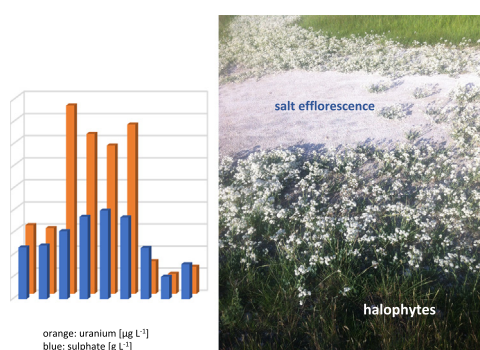
Regina Krachler *, Rudolf Krachler, Fadime Gülce, Bernhard K. Keppler, Gabriele Wallner

University of Vienna, Faculty of Chemistry, Institute of Inorganic Chemistry, Währingerstrasse 42, A-1090 Vienna, Austria

HIGHLIGHTS

- Uranium isotopes were analyzed in sediment pore waters of Lake Neusiedl.
- Halophyte *Salicornia prostrata* was used as an indicator of sodium sulphate.
- Halophyte *Lepidium cartilagineum* was used as an indicator of sodium carbonate.
- Elevated uranium concentrations were associated with high sulphate concentrations.
- $^{234}\text{U}/^{238}\text{U}$ activity ratios were near unity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 26 December 2017
Received in revised form 21 March 2018
Accepted 21 March 2018
Available online 28 March 2018

Editor: F.M. Tack

Keywords:

Uranium isotopes
Natural uranium contamination
Groundwater
Pore waters

ABSTRACT

The goal of the present investigation was to measure $^{234}\text{U}/^{238}\text{U}$ activity ratios in pore waters of Lake Neusiedl, Austria, in order to learn more about uranium in groundwaters of the Lake Neusiedl/Seewinkel region. Pore waters of waterlogged sediments (at 1 m depth) in the littoral zone of Lake Neusiedl were analyzed. The pore water samples were collected in the National Park Lake Neusiedl/Seewinkel from pristine sites that were not influenced by neighboring fertilized fields or vineyards. Uranium isotopes were extracted from 1.5 L of sediment pore water and measured by α -particle spectrometry. Uranium concentrations were found to be unexpectedly high (up to $853 \mu\text{g L}^{-1}$) especially in pore waters of salt-rich locations. $^{234}\text{U}/^{238}\text{U}$ activity ratios were between 0.91 and 1.09 for all pore water samples, irrespective of their origin from the east or west littoral zones of the lake. Uranium and mineral salts concentrations were strongly correlated. ^{222}Rn concentrations were low (between 22 and 42 Bq L^{-1}). The results provide insight into the high degree of mobility of U(VI) in sedimentary environments, in the presence of migrating Na_2SO_4 -type saline waters.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Uranium is a ubiquitous radionuclide in the Earth's crust, commonly deposited as a component of secondary minerals due to weathering of igneous parent materials. The major part of uranium in soils and sediments occurs as insoluble U(IV) minerals, e.g., uraninite, which may

be associated with volcanic rocks, black shales, or granites (Nolan and Weber, 2015; Khattab et al., 2017). Sulphate- and iron-reducing bacteria reduce U(VI) to U(IV) (Duff et al., 1997) and this mechanism operates in anoxic sediments. The remobilization of uranium is governed by the formation of the hydrated cation UO_2^{2+} . Exposure of U(IV) minerals to oxidizing groundwater may lead to oxidative dissolution, producing dissolved U(VI) species (Nolan and Weber, 2015). However, UO_2^{2+} strongly adsorbs to sedimentary matrices. The ability of clay minerals, carbonates, iron hydroxides and other minerals to adsorb U(VI) is well

* Corresponding author.
E-mail address: regina.krachler@univie.ac.at (R. Krachler).

documented (Davis et al., 2004). Additionally, the uranyl cation UO_2^{2+} can substitute for Ca^{2+} in mineral lattices, resulting in uranium contents in calcium phosphates such as apatite (Starinsky et al., 1982; Rakovan et al., 2002), or calcium carbonates such as calcite and dolomite (Sturchio et al., 1998; Kelly et al., 2003). On the other hand, the presence of dissolved complexing agents in the pore water phase counteracts adsorption and leads to the formation of soluble U(VI) species. Under alkaline oxidizing conditions, soluble uranyl carbonate complexes, such as $\text{UO}_2(\text{CO}_3)_2^{2-}$ predominate. At lower pH and in saline groundwaters, soluble complexes of UO_2^{2+} with sulphate (Hennig et al., 2008), phosphate (Bachmaf et al., 2008), or fulvic acids (Esteves da Silva et al., 1996; Alberti et al., 2007), can be responsible for elevated uranium concentrations. In most natural waters uranium is present at concentrations between 0.1 and $10 \mu\text{g L}^{-1}$ (Hosseini-Bandegharaei et al., 2013), although concentrations exceeding 1 mg L^{-1} can occur in waters associated with uranium ore deposits.

Uranium in drinking water poses an environmental health risk particularly to children, due to its nephrotoxic and osteotoxic potential (Frisbie et al., 2013; Steffanowski and Banning, 2017). To be on the safe side, Austria established a legal limit of $15 \mu\text{g L}^{-1}$ uranium in its Drinking Water Ordinance. Groundwater is a major source for drinking water supply, therefore, in 2013, the Austrian Federal Environmental Agency measured uranium at numerous ($N = 1940$) groundwater monitoring sites throughout Austria (Wemhöner et al., 2015). In most regions, very low concentrations were found. Uranium concentrations above the legal limit of $15 \mu\text{g L}^{-1}$ were directly related to geogenic sources, e.g. granites and gneisses in the Central Alps and in the Bohemian Massif.

With one remarkable exception: In the Seewinkel Plain, located to the East of Lake Neusiedl, a large fraction of the groundwater samples collected by the Austrian Federal Environmental Agency exceeded the Austrian legal limit of $15 \mu\text{g L}^{-1}$. In this region, geogenic sources have been thought to be unlikely. Underlying sediments of Tertiary age, which form the aquitard, are covered by Quaternary sediments of Late Pleistocene age, predominately fluvial sandy gravels. The uranium content of these Quaternary deposits, which constitute the aquifer, is minimal (Berka et al., 2014).

The radioactive decay of uranium progeny releases radon gas, which is highly mobile and has a short half-life of 3.8 days. The Austrian Federal Environmental Agency performed measurements of ^{222}Rn at groundwater monitoring sites throughout Austria (Berka et al., 2014) and could show that ^{222}Rn concentrations correlate well with uranium in the groundwater as well as with uranium in the adjacent rocks and sediments. Berka et al. (2014) suggested that elevated ^{222}Rn levels in the groundwater can be used as an indicator of elevated uranium contents in rocks and sediments of an investigated area. This hypothesis is based on the assumptions that the ^{222}Rn level in the groundwater is related to the level of ^{226}Ra in the surrounding sediment matrix and that uranium-bearing minerals in rocks and sediments usually contain increased amounts of radium (Liatsou and Pashalidis, 2016). Low ^{222}Rn values point therefore to low uranium contents in the sediments which constitute the aquifer. The measurements by Berka et al. (2014) revealed that the shallow groundwaters of the Seewinkel Plain are characterized by low concentrations of ^{222}Rn . Hence these authors suggested that the elevated uranium concentrations $>15 \mu\text{g L}^{-1}$ found by Wemhöner et al. (2015) might be caused by human activities (phosphate fertilizers) rather than by elevated uranium contents in the surrounding sediments.

While the Seewinkel Plain is not influenced by mining or industrial zones, it is used intensively for agriculture. Consequently, a possible anthropogenic entry path for uranium is the use of uranium containing phosphate fertilizers. In phosphate fertilizers, uranium can be found in varying concentrations from 2 to 200 mg kg^{-1} , depending on the uranium content in the initial rock phosphates (Liesch et al., 2015). Activity ratio $^{234}\text{U}/^{238}\text{U}$ in fertilizer is 1.00 ± 0.05 due to its origin from phosphate rocks (Zielinski et al., 2000).

Natural uranium consists of three alpha radioactive isotopes, 99.2745% of ^{238}U (half-life 4.468×10^9 y), 0.7200% of ^{235}U (half-life 7.04×10^8 y), and 0.0054% of ^{234}U (half-life 2.455×10^5 y). The average uranium concentration in Earth's crust is about 2.6–2.8 mg kg^{-1} (Hu and Gao, 2008). Uranium isotopes ^{234}U and ^{238}U are in many cases not present in radioactive equilibrium in the aquatic environment. Radioactive decay of a ^{238}U atom in a crystalline mineral phase causes a “kickback” to the newly created isotope. The recoil atom ^{234}Th is excited out of its crystal lattice site into an interstitial position and its progeny ^{234}U is therefore more liable to be oxidized to the hexavalent stage and can be leached into the water phase more rapidly than its precursor nuclide ^{238}U . Accordingly, natural waters tend to show $^{234}\text{U}/^{238}\text{U}$ activity ratios >1 (Zielinski et al., 2000; Boryło and Skwarzec, 2014). Most notably, in groundwaters, this isotopic activity ratio may go up to 20 and above (Carvalho and Fajgelj, 2013).

As mentioned above, a geogenic source for uranium seems unlikely in the Seewinkel Plain given the low ^{222}Rn concentrations in the shallow groundwaters. However, the uranium could be more mobile in the sediments than previously thought. Berka et al. (2014) hypothesized that uranium containing saline waters may ascend locally from deep strata of Tertiary age and infiltrate into the overlying shallow drinking water aquifers of the Seewinkel Plain, causing elevated uranium levels. The existence of a deep saliferous horizon in the Lake Neusiedl/Seewinkel region has been proven as early as 1955 when well drilling for drinking water came upon a mineral water horizon in 121.4 m depth near the village of Mörbisch on the west shore of Lake Neusiedl. The total salinity of this mineral water was about 30 g L^{-1} . The salts found in the mineral water were mainly sodium sulphate, sodium chloride and sodium hydrogen carbonate (Fritsch and Tauber, 1959) while uranium has never been analyzed. These authors suggested a rich and extensive mineral water deposit underneath Lake Neusiedl and most of the Seewinkel Plain. However, up to present, no evidence was found to prove that brines are ascending from these deep strata to superficial groundwater bodies.

According to the hypothesis by Berka et al. (2014) that ascending brines may occur in some places, and that they might be a source of uranium, we decided to analyze sediment pore waters (at 1 m depth) from salt-rich locations in the littoral zone of Lake Neusiedl. We chose sampling stations in pristine natural landscapes uninfluenced by cultivated fields and vineyards in order to exclude phosphate fertilizers as a possible source of uranium. The goal was to measure uranium concentrations, $^{234}\text{U}/^{238}\text{U}$ activity ratios and ^{222}Rn , ^{226}Ra , and ^{210}Po activities in the sediment pore waters.

2. Materials and methods

2.1. Study area and sampling sites

The Neusiedler See-Seewinkel National Park was established in 1993. It comprises Lake Neusiedl and the saline meadows and salt pools of the Seewinkel Plain. The about 50 astatic saline pools are filled with water in spring and shrink or disappear entirely in periods of drought in summer. The salt pools and saline meadows are essential factor for the thriving of a unique flora and fauna in the National Park. Several maritime littoral plant species e.g. the halophyte *Salicornia prostrata* grow in this region, despite the long distance from the European coast (Király et al., 2013).

Lake Neusiedl is situated between the Eastern Alps and the Little Hungarian Plain (Kisalföld). Today's morphology of the region is controlled by Latest Pliocene–Quaternary tectonic subsidence. The tectonic processes in this area result from the continental collision of the Adriatic and Eurasian Plates (Horváth et al., 2006). Lake Neusiedl currently has an area of approximately 285 km^2 (Schmidt and Csaplovics, 2011; Király and Márkus, 2011) and a lake level at 115.5 m a.s.l. (Bácsatyai et al., 1997). The entire lake is very shallow (1–1.7 m maximum) with the deepest part of the lake bottom at around 113 m a.s.l. (Bácsatyai

Download English Version:

<https://daneshyari.com/en/article/8860241>

Download Persian Version:

<https://daneshyari.com/article/8860241>

[Daneshyari.com](https://daneshyari.com)