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## Uranium in different samples from Eastern Macedonia – a case study

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### Abstract

Content of uranium in the Sasa tailings dam material varies from 1.8 to 5.5 mg kg<sup>-1</sup>. Sasa tailings dam failure cause discharge of material in the Lake Kalimanci. The uranium content in surficial lake sediments in years, before the tailings dam failure varied from 2.4 to 5.4 mg kg<sup>-1</sup> and after the failure from 3.6 to 10.4 mg kg<sup>-1</sup>. Meanwhile Lake Kalimanci water contains lower concentrations of uranium (0.9-1.1 µg ml<sup>-1</sup>). Water from Lake Kalimanci is being used for irrigation of the nearby Kochani valley, where the uranium content in soils varies from 73 to 182 mg kg<sup>-1</sup>.

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### 1. Introduction

The toxicity of uranium to humans and other living organisms has been of interest since the 1800s<sup>1</sup>. The vast majority of uranium that is free in the environment, and thus a possible source of human exposure, comes from the use of depleted uranium munitions<sup>2</sup>. The next main source of uranium exposure is presented by uranium rich deposits or other metal deposits connected with uranium. Historically, most epidemiology connected with uranium mining has focused on mine workers and radon exposure, although a smaller emerging literature has begun to form

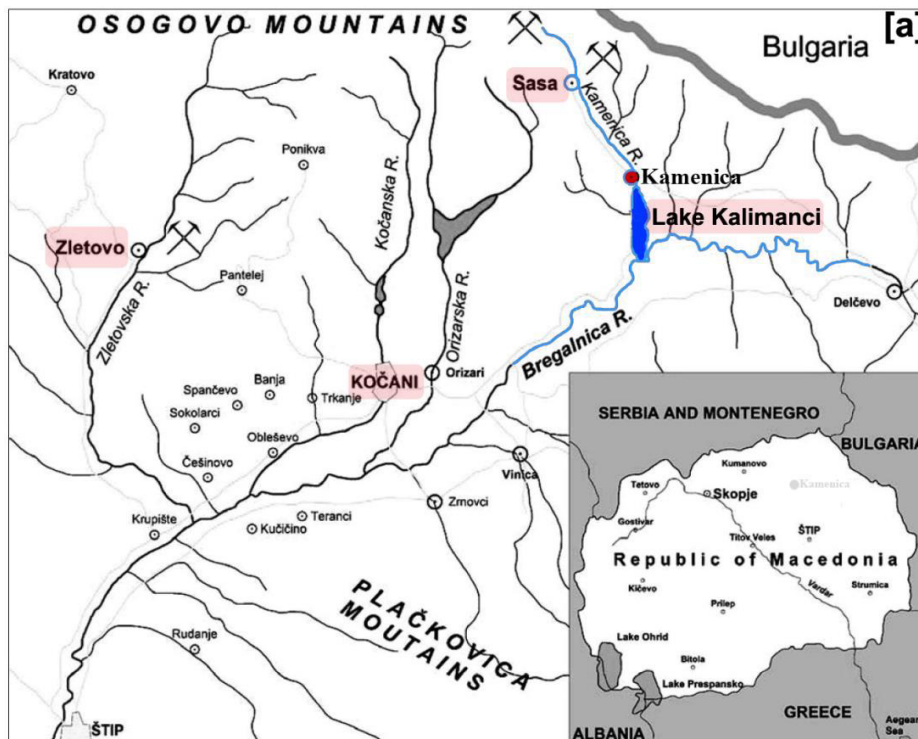
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around environmental exposure in residential areas and nearby (uranium and other metal) mining facilities<sup>3</sup>. Humans can be exposed to uranium by inhaling dust in the air or by ingesting contaminated water and food. Generally concentrations of uranium in the air are very low, but long term exposure can also lead to serious health effects. Uranium has toxic effects functions on the cardiovascular system, liver, kidneys, muscles and nervous system, but can also damage skin, bones and other parts of the human body<sup>3,4</sup>. Uranium, after entering human body, is usually absorbed from the intestine or lungs, enters the bloodstream and is rapidly deposited in the tissues (predominantly kidney and bone) or is excreted in the urine.

Serbo-Macedonian Masiff contain two main ore deposits in the Osogovo Mountains, the Sasa-Toranica and Zletovo-Kratovo ore deposits, which are connected by the same geology catchment (Fig. 1a-b). It comprises highly metamorphic rocks containing gneiss, micas, amphibolites ilvaite skarns and schists. A typical mineral assemblage around the Sasa Mine area is represented by ore minerals: pyrite, galena, sphlareite, sometimes chalcopyrite and traces of ceruzite, anglesite and malachite. Next to the active Sasa mine, uranium origin can be also linked to the small uranium deposit in the south-west slopes of Osogovo Mountains which extends into the SMM. Uranium deposit in the Zletovska Reka region is related to Tertiary calc alkaline volcanics and belongs to low- to medium-temperature hydrothermal uranium deposits with small admixtures of other ore minerals<sup>5</sup>. A concentration of uranium in different granitoid complexes from SMM ranges from 2.8 to 10 mg/kg<sup>6</sup>. The present study was conducted over a wide area in Eastern FYR Macedonia, where several active mines are located. The main objective of this research was to evaluate concentrations of uranium in different samples from a wide area in NE FYR Macedonia and to assess the possible effects of uranium on human health.



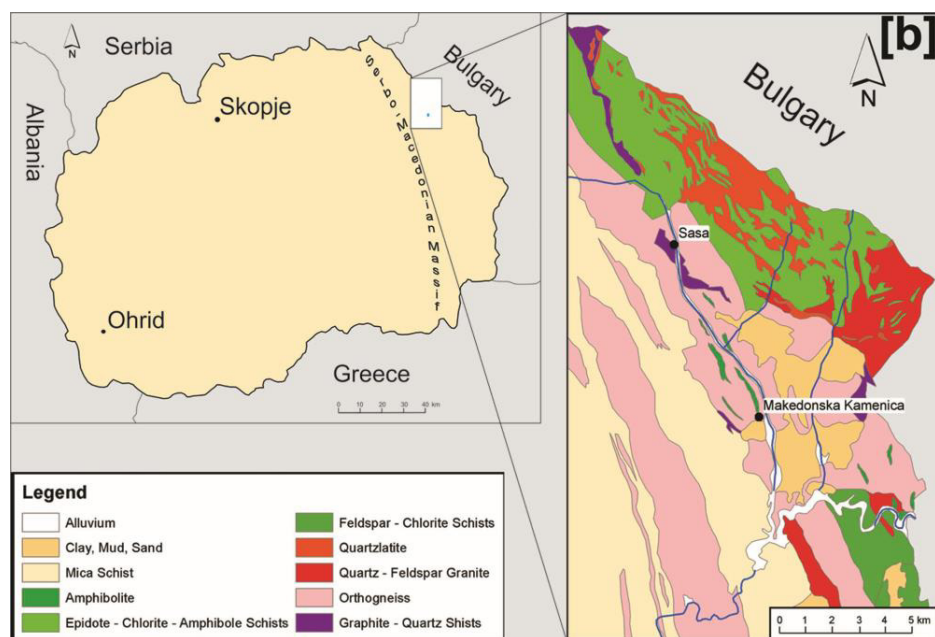


Fig.1. (a) Study area; (b) basic geological composition of research area.

## 2. Materials and methods

### 2.1 Sampling and sample preparation

Six surficial samples from the Sasa tailings dam were taken in October 2003. The surficial samples were collected in plastic bags and stored in the laboratory at 4°C. The samples were dried at 50°C for 48 hours. They were then sieved through a 0.315 mm polyethylene sieve and homogenised by a mechanical agate grinder to a fine powder for further analysis. Surficial sediment samples from Lake Kalimanci were taken before the accident in August 2001. The sampling collection was resumed in September 2007 four years after the accident happened. The sediment pH ranged between 5.5 and 7.5, and redox potential ranges were between -325 mV and +180 mV. The samples were collected with plastic corers (a tube 10 cm long with a 7 cm internal diameter), and were tightly packed into self-locking polyethylene bags. Water samples from Lake Kalimanci were collected at all twelve sampling sites at the same time as the fish collection. Water samples were filtered using a hand-pump on site through a 0.45 µm membrane filter paper into pre-cleaned sample bottles. After immediate acidification with concentrated HNO<sub>3</sub>, the samples were stored in a cooling box (< 4°C) until analysis. The sampling of the paddy soils from the Kochani valley was carried out between the villages Orizari and Krupište in autumn 2005. The paddy soils were sampled using a plastic spade to avoid any metal contamination and each sample comprised a composite of five sub-samples taken within 1 x 1 m<sup>2</sup> square.

### 2.2 Analyses

The geochemical analysis of the Sasa tailings dam material, the Lake Kalimanci surficial sediments and soil samples were processed at the commercial ACME Laboratories in Vancouver, Canada, using inductively coupled plasma mass spectrometry (ICP/MS). The accuracy and precision were assessed using international reference materials. A sequential extraction analysis was also applied in ACME Laboratories, to reveal the mobility and bioavailability of U in lake sediments.

## 3. Results and discussion

The north-east FYR Macedonia region is very rich in numerous metal deposits, among which Pb-Zn mines are currently heavily exploited. Next to lead and zinc, copper and gold are also very important in this region. Pb-Zn mines in north-east FYR Macedonia are some of the largest in Europe and consequently produce vast tailing dams. Due to wind transfer of the tailings dam material all over the Makedonska Kamenica and Kochani valley regions the U content was determined for such material. Results revealed that U content in Sasa tailings dam material varies from 1.8 to 5.5 mg/kg. In the 2003 the Sasa tailings dam failure occurred and caused an intensive flow of waste material through the Kamenica River valley and deposited in Lake Kalimanci. Since water from this lake is used for the irrigation of paddy fields in Kochani valley, sediments before and after the failure were studied. The U content in surficial sediments from Lake Kalimanci ranged from 2.4 to 5.4 mg/kg before the tailings dam collapse (Fig. 2a) and from 3.6 to 10.4 mg/kg after the failure (Fig. 2b). Meanwhile a sequential extraction procedure revealed that the majority of U was found to be associated with the exchangeable fraction (F2) (Fig. 3). This indicates that U is highly mobile and bioavailable under normal conditions.

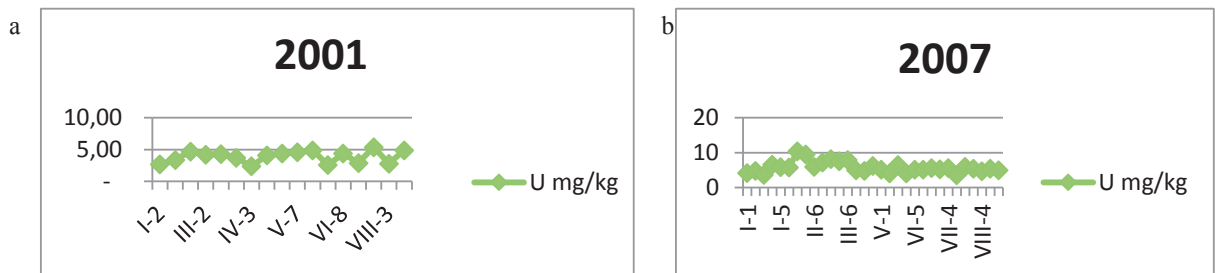


Fig. 2. (a) Uranium content in the surficial lake sediments before the tailings dam failure (2001); (b) Uranium content in the surficial lake sediments after the tailings failure (2007).

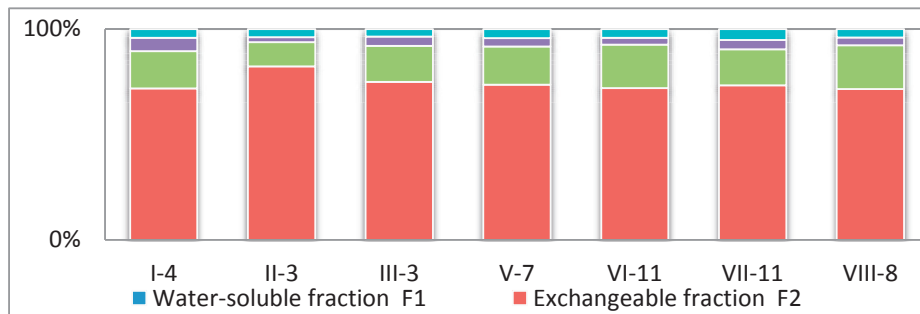


Fig. 3. Percentage U removed after each step of the sequential extraction procedure applied to sediments from Lake Kalimanci.

Lake Kalimanci waters were also examined and results showed low concentrations of U ( $0.9 - 1.1 \mu\text{g/ml}$ ). As mentioned above, water from Lake Kalimanci is being used for the irrigation of nearby agricultural area, thus U content in soils from Kochani valley was determined, and found to vary from 73 to 182 mg/kg. This is much higher than in the lake sediments and water. U thus originates from other sources than the lake environment itself, but is most likely correlated with the small scaled uranium deposits in the south-west slopes of Osogovo Mountains, near Zletovska Reka region (Fig. 1a).

#### 4. Conclusions

The Sasa tailings dam failure occurred in year 2003 and the majority of the waste material was subsequently discharged through the Kamenica River Valley to Lake Kalimanci. Uranium concentrations defined in the Sasa tailings dam material varies from 1.8 to 5.5 mg kg<sup>-1</sup>. The uranium content in surficial lake sediments measured before the tailings dam failure ranged from 2.4 to 5.4 mg kg<sup>-1</sup> and from 3.6 to 10.4 mg kg<sup>-1</sup> after the accident. A sequential

extraction procedure revealed that the majority of uranium was associated with the exchangeable fraction (F2), indicating high mobility and bioavailability of uranium under normal environmental conditions. Meanwhile, Lake Kalimanci water contains lower concentrations of uranium ( $0.9\text{--}1.1\ \mu\text{g ml}^{-1}$ ). Water from Lake Kalimanci is being used for irrigation of the nearby Kochani valley, where the uranium in soils varies from 73 to 182 mg kg<sup>-1</sup>.

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