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Recent measurements of $^{234}U/^{238}U$ isotope ratio in spring waters from the Hadzici area

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ABSTRACT

The Hadzici area has become interesting for investigation since depleted uranium ammunition had been employed in 1995 during the NATO air strike campaign in Bosnia and Herzegovina. The purpose of this study is to determine uranium concentration and $^{234}U/^{238}U$ activity ratio in the spring waters of this area and to investigate their relationship, as well as spatial variations. The spring water samples were taken at 18 sites in total. For the determination of uranium radioisotopes, radiochemical separation procedure followed by alpha-particle spectrometry was applied. Uranium concentration in analyzed waters range from 0.15 to 1.12 μg/L. Spring waters from carbonate based sediments have a lower uranium concentration of between 0.15 and 0.43 μg/L, in comparison to waters sampled within sandstone-based sediments ranging from 0.53 to 1.12 μg/L. Dissolved uranium shows significant spatial variability and correlation with bedrock type confirmed by Principal Component Analysis and Hierarchical Cluster Analysis. The majority of the analyzed waters have a $^{234}U/^{238}U$ activity ratio ranging from 1.02 to 1.90, of which half of the results range between 1.02 and 1.16. No apparent depleted uranium (DU) contamination was observed, as $^{234}U/^{238}U$ activity ratio is dependent on geochemical conditions in the environment. Even though the tested spring waters demonstrate significant variability in uranium concentration, $^{234}U/^{238}U$ activity ratio and ^{234}U excess, waters with similar uranium isotopic signatures are observable within the region. The guidelines on the spatial redistribution of dissolved uranium (corresponding to ^{238}U mass concentration), along with $^{234}U/^{238}U$ activity ratios were provided by the Inverse Distance Weighting (IDW) method. Waters having similar isotopic signature have been delineated.

1. Introduction

Uranium is a naturally occurring radioactive element, widely distributed in nature. It is found in significant concentrations in many varieties of rocks as well as in ground and surface waters, due to rock water interactions. The average concentration of uranium in the Earth's crust is 3 mg/kg (Bleise et al., 2003). Uranium concentration in ground and surface waters is three orders of magnitude lower, approximately 1 μg/L, although it can range from 0.001 to 1000 μg/L (Osmond et al., 1983). Numerous factors have an influence on uranium concentration in natural water, such as type of the rocks of the aquifier, redox conditions, acidity/alkalinity, CO_2 and O_2 concentration, temperature, presence of inorganic and organic compounds, colloids, etc. (Chabaux et al., 2008; Porcelli, 2008). A notable feature of dissolved uranium in natural water is an enhanced $^{234}U/^{238}U$ activity ratio. Typically, the $^{234}U/^{238}U$ activity ratio in natural water varies from 1 to 2, but it can range up to 30 in extreme cases (Osmond et al., 1983). Commonly observed fractionation and disequilibrium between ^{234}U and ^{238}U in water is a result of nuclear recoil effects (Fleischer and Raabe, 1978; Osmond et al., 1983) and extensive rock/water interactions. The combination of uranium concentration and $^{234}U/^{238}U$ activity ratio, widely described as the uranium isotopic signature, has been generally used for the characterization of ground and surface water (Osmond et al., 1983; Riotte and Chabaux, 1999; Abdul-Hadi et al., 2001; Dabous and Osmond, 2001; Dabous et al., 2002; Paces et al., 2002; Cizdziel et al., 2005; Bonotto, 2006; Reyes and Marques, 2008; Chkir et al., 2009; Hadj Ammar et al., 2010). For the purpose of evaluating groundwater aquifer and possible mixing of the water, a diagram of $^{234}U/^{238}U$ activity ratio vs. inverse uranium concentration is used (Osmond et al., 1983). Typically, this diagram exhibits a linear trend extending from the lower left indicating

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a contribution of the concentrated leachate of the host rock due to extensive weathering and possibly shallow water, to the upper right were recoil and/or preferential leaching of ^{234}U prevail, contributing to higher $^{234}U/^{238}U$ activity ratio (Dabous, 1994). In addition, ^{234}U excess, calculated by the expression: ^{234}U excess = (AR-1)*C_U, where AR is $^{234}U/^{238}U$ activity ratio, and C_U is uranium mass concentration in μg/L (Cowart and Osmond, 1980), can be used to identify geochemically similar waters (Abdul-Hadi et al., 2001; Dabous and Osmond, 2001; Cizdziel et al., 2005).

The purpose of this study is to determine uranium concentration and $^{234}U/^{238}U$ activity ratios in the spring waters of the Hadzici area, and to investigate their relationship, as well as spatial variations. In the Hadzici area depleted uranium ammunition had been employed in 1995 during the NATO air strike campaign in Bosnia and Herzegovina. Since then several investigations on natural uranium and the presence of the depleted uranium in the environment, and in particular groundwater, have been conducted (UNEP, 2003; Jia et al., 2006; Carvalho and Oliveira, 2010). We expanded the number of the sampling sites in order to obtain more detailed information on uranium in groundwater of the investigated area.

2. Material and methods

2.1. Description of study area

The investigated area lies in the Hadzici region, approximately 15 km west of the Bosnian capital Sarajevo, and covers approximately 25 km^2. Within the investigated area lies a former tank repair facility where DU ammunition was employed during air force attacks in 1995. According to available data, approximately 10,000 30-mm projectiles, or nearly 3 tonnes of DU, were used (Bleise et al., 2003). Hadzici and the tank repair facility lie in the valley of the Zujevina River at an altitude of approximately of 500 m, surrounded by hills up to between 1000 and 1500 m above sea level. Many springs occur in the area, typically on the slopes of the hills. Those springs, used by the local inhabitants for water supply, are protected by custom-made concrete boxes. The main watercourse in the area is the Zujevina River, which runs through Hadzici from south to north. Vihrica brook, its left tributary, drains through the tank repair facility running from the west. Another important watercourse, the Zunovnica River, joins the Zujevina in the downstream section of the river. The geological composition of the investigated area is represented by sediments of the Lower and Upper Triassic, Upper Cretaceous and Quaternary (Skopljak et al., 2006) (Fig. 1). The central part of the investigated area, stretching east – west, is comprised of sandstones, argillites, clayey marls and sandy limestones. Carbonates of dolomite, dolomite limestone and limestone are distributed on the north and south. Sediments of the Ladinian, represented by volcanic-sedimentary formation, are situated in the smaller area in the northern part, while sediments of the flysch of the Upper Cretaceous has a significant distribution in the north-east part of the area. Quaternary deposits in the valley of Zujevina and Vihrica rivers are represented by sediments such as debris, gravel and sand. The sediments of the Lower Triasic are characterized as poorly permable rocks of the fractured porosity, comparing to well permable rocks of cavernous-fractured porosity of carbonate deposits of Middle Triasic, which makes up the main, deep karst aquifier of this area (Skopljak et al., 2006). Soil composition of the area consists mainly of Dystric and Humic Cambisols,

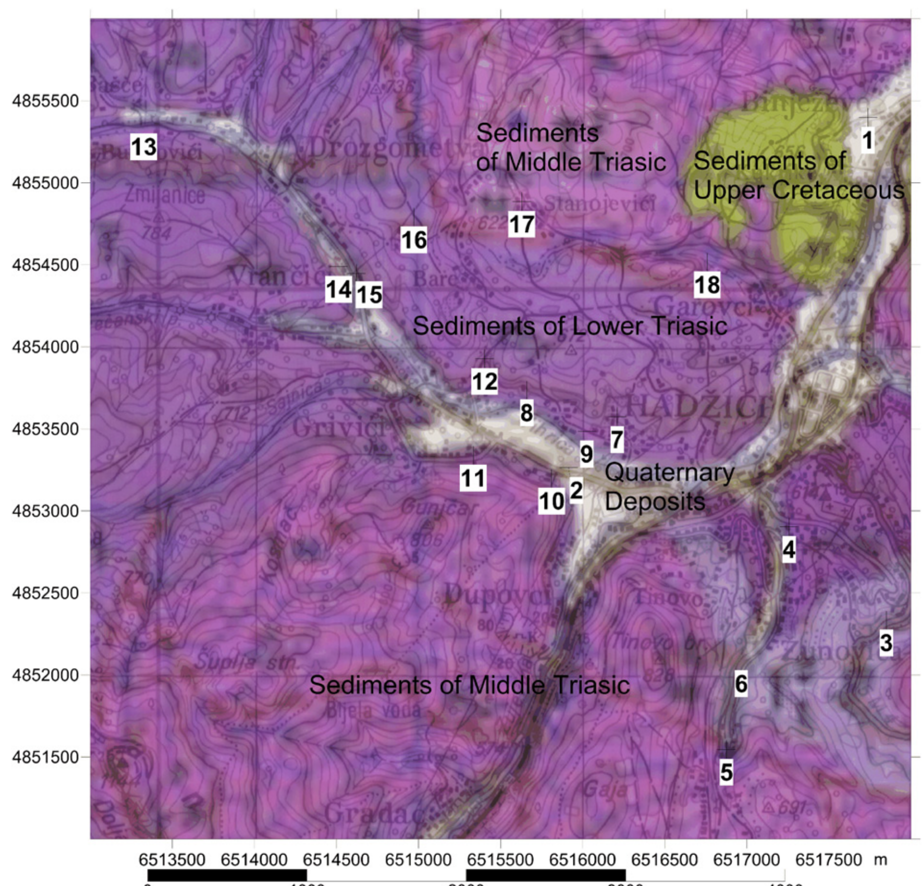

Fig. 1. Geological map of the Hadzici area including sampling sites (Gauss-Krüger cartographic projection).