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Uranium in Kosovo's drinking water

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HIGHLIGHTS

- We report the uranium concentration in 951 drinking water samples from Kosovo.
- The water samples were analyzed with inductively coupled plasma mass spectrometry.
- 2.6% Of analyzed water samples exceeded WHO drinking water guidelines of 30 μg L^{-1}.
- 44% Of the water samples exceed the recommended concentration for babies (2 μg L^{-1}).
- Our data provide valuable information for the population and authorities of Kosovo.

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ABSTRACT

The results of this paper are an initiation to capture the drinking water and/or groundwater elemental situation in the youngest European country, Kosovo. We aim to present a clear picture of the natural uranium concentration in drinking water and/or groundwater as it is distributed to the population of Kosovo. Nine hundred and fifty-one (951) drinking water samples were analyzed by inductively coupled plasma mass spectrometry (ICPMS). The results are the first countrywide interpretation of the uranium concentration in drinking water and/or groundwater, directly following the Kosovo war of 1999. More than 98% of the samples had uranium concentrations above 0.01 μg L^{-1}, which was also our limit of quantification. Concentrations up to 166 μg L^{-1} were found with a mean of 5 μg L^{-1} and median 1.6 μg L^{-1} were found. Two point six percent (2.6%) of the analyzed samples exceeded the World Health Organization maximum acceptable concentration of 30 μg L^{-1}, and 44.2% of the samples exceeded the 2 μg L^{-1} German maximum acceptable concentrations recommended for infant food preparations.

1. Introduction

In March, 1999, the North Atlantic Treaty Organization (NATO) aircraft fought a war for humanitarian purposes against ethnic cleansing in Kosovo, and fired over 30000 penetrators containing depleted uranium (DU) metal in 85 locations throughout Kosovo (land size of 10887 km^2, with approximately 2 million inhabitants) (UNEP, 2001). Since then, concerns over the environmental uranium pollution and health hazard issues within the territory of Kosovo have been raised.

As a consequence of the latest Balkan events, environmental research in Kosovo has been focused on uranium radioactivity, mainly from depleted uranium. According to United Nations of Environmental Protection (UNEP) the DU in Kosovo is possibly masked within the soil, which later could reach the water table and enter drinking water wells. In such cases, it is estimated that the uranium concentration in groundwater is likely to be below 25 μg L^{-1} (UNEP, 2001). Subsequent to the UNEP monitoring assessment, Durante and Pugliese (2003) calculated, via a mathematical model, the radiological risk assessments of residual DU in Kosovo. They hypothesized that the contamination of uranium could be a future hazard in Kosovo that can only be evaluated via groundwater studies in later years. Their hypothesis was confirmed by the studies of Shimmack et al. (2005, 2007) showing leaching of DU into soil. After many years of continues monitoring of DU into soil, Shimmack et al. (2007) found a dramatic increase of leaching over years (factor of more than 100), and as a result, stipulated further investigation of the groundwater in areas where the DU munitions was fired. Additionally, other post-war uranium studies in Kosovo have raised similar concerns that the uranium would enter the food supply and groundwater some years later (Sansone et al., 2001; Jia et al., 2004; Mellini and Riccobono, 2005; Oeh et al., 2007). The uranium solubility in the groundwater depends on the water's chemical profile and it is much higher under oxidizing conditions than reducing conditions (Frosberg, 2000).

To date most of the studies of Kosovo's uranium situation (Di Lella et al., 2003, 2004, 2005; Sansone et al., 2001; Danesi et al., 2003; Loppi et al., 2004; Jia et al., 2004) have focused mainly on bio-monitoring the eleven sites where UNEP had conducted its

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preliminary assessment in 2001 (UNEP, 2001). Other studies focused on DU penetrators such as smear and dart (Jia et al., 2004; Mellini and Riccobono, 2005). The remainder of Kosovo's territory is not investigated for natural uranium contamination. Moreover, the previous scientific research in Kosovo's uranium pollution was mainly conducted immediately after the war with samples collected and investigated no later than 2001. Danesi et al. (2003) presents high surface soil uranium contaminations up to 4000 mg kg^{-1}, yet concludes that even though they find high concentration of uranium, the few soil samples taken intentionally at the hot spots are not representative for the environmental uranium contamination in Kosovo. Besides, it was suggested that for more thorough geochemical monitoring, the uranium contamination in Kosovo should be measured at different places and not only in the battlefield areas in southwest Kosovo (Mellini and Riccobono, 2005). Consequently, Durante and Pugliese (2003), Mellini and Riccobono (2005) and lately Shimmack et al. (2007) had suggested not only continuity on uranium concentration monitoring, but also long-term monitoring of water pollution in Kosovo.

The aim of our study was to analyze the elemental concentrations in drinking water samples and assess a potential risk for the population. Therefore, we determined the natural elemental concentrations in drinking water samples covering Kosovo's territory with inductively coupled plasma mass spectrometry (ICPMS). In this paper we discuss only natural uranium concentrations while results of other elements were published elsewhere (Berisha and Goessler, 2013). Additionally, future work on the isotopic distribution of uranium and its anthropogenic nature in drinking water and/or groundwater will be conducted.

2. Uranium and its health effects

Uranium is a naturally occurring element found in rocks, soil, water and air. The natural uranium is a mixture of three different isotopes, ^{238}U, ^{235}U and ^{234}U, with abundances of 99.3%, 0.72% and 0.0054%, respectively. The depleted uranium, whose chemical toxicity and environmental behavior is similar to natural uranium, usually consists of 99.8% ^{238}U, 0.21% ^{235}U and 0.001% ^{234}U (Betti, 2003; Meinrath et al., 2003). The main uranium sources are uraninite (UO_2), pitchblende (U_3O_8), carnonite ($K(UO_2)_2(VO_4)_23H_2O$), phosphate minerals and lignite (Stalder et al., 2012). Uranium has low specific activity and as a result its chemotoxicity is of much greater concern (Stalder et al., 2012). Independent of the source, depleted or natural, uranium is a toxic chemical (Betti, 2003). Biologically and chemically the two are equivalent, yet depleted uranium, which consists of mainly ^{238}U, has roughly half of the natural uranium radioactivity (Auvinen et al., 2002). Uranium can be present in drinking water and/or groundwater due to natural deposits, emissions from nuclear power productions, combustion of coal and fuels as well as use of phosphate fertilizers (WHO, 2005; Birke et al., 2010). Although the uranium concentration in drinking water depends on the geochemical situation of a region, its concentration is difficult to predict when the groundwater streams are not known (Stalder et al., 2012).

A comprehensive explanation of natural environmental uranium concentration ranges, forms of ingestion and inhalation, body absorption and excretion, and other radiological and chemical aspects of uranium are explained and presented by Oeh et al. (2007). Elevated uranium concentrations in drinking water have been associated with many epidemiological studies such as leukemia, stomach and urinary track cancer as well as kidney toxicity, renal, bone damage and increased diastolic and systolic blood pressure, yet a clear understanding of the human toxicity from uranium elevated drinking waters has not been achieved nor associated (Zamora et al., 1998, 2009; Auvinen et al., 2002, 2005; Kurttio et al., 2002; Kurttio et al., 2005; Kurttio et al., 2006; Prat et al., 2009). Auvinen et al. (2002) investigated a possible connection of uranium in drinking water and leukemia. They could not find an association to ingested natural uranium. Therefore, they concluded that unless exposed from DU in massive doses, it is unlikely to show any health effects. Moreover, Auvinen et al. (2002) pointed out that the uranium health effects could depend on the environmental pathway as well as the form of exposure. Contrary, that same year Kurttio et al. (2002) reported that the elevated uranium concentrations are associated with the increased uranium concentration in urine, increased systolic and diastolic blood pressure and also confirmed that uranium in drinking water effects the kidney functioning. A recent study (Lariviere et al., 2012), found a strong correlation between uranium concentration in drinking water and uranium in bone, suggesting that bone are a good indicator of uranium exposed via ingestion of drinking water. Therefore, such studies trigger further assessment of uranium adverse health effects to humans and/or the environment for countries where elevated uranium concentration in drinking water has been observed.

3. Materials and methods

Between June 2009 and March 2010, 951 drinking water samples from private – bored wells, naturally flowing artesian water, pumped – drilled wells and public water sources (tap water) were collected throughout Kosovo (Fig. 1). The samples were collected in 50 mL polyethylene vials, acidified with trace metal grade 67–70% nitric acid (Fisher Scientific, Germany) to pH < 2, given a field name, packed, recorded on the field log book and within a month, transported to the laboratory in Austria for analysis.

The concentration of 32 elements (Li, Be, B, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Te, Ba, Tl, Pb, Bi, Th, U) in drinking water was analyzed with inductively coupled plasma mass spectrometry (ICPMS, Agilent 7500ce, Agilent Technologies, Waldbronn, Germany) equipped with a Mira Mist nebulizer (Burgener Research Inc, Ontario, Canada) (Berisha and Goessler, 2013). Uranium was analyzed at m/z 238. For control of instrument stability, lutetium (CPI International, Santa Rosa, USA) was continuously added online as an internal standard. Instrument optimization for stable signal, high sensitivity and low background was performed daily with a tuning solution.

The reference materials used for quality control purposes were NIST SRM 1643d $n = 7$ (NIST, Gaithersburg, MD, USA) and IFA Test Systems $n = 71$ (BOKU, Tulln, Austria) reference water with certified elemental concentrations. In all reference water samples, the uranium concentration was less than 0.005 μg L^{-1}. In addition, blank, drift control and duplicate samples were analyzed at regular intervals throughout the sample analysis. Calibration standards of uranium with a concentration range of 0.01–100 μg L^{-1} were prepared with ultrapure water from the Milli-Q purification system in 10 mL polystyrene vials via dilution of 1000 mg L^{-1} Merck VI multi-elemental standard solution.

Surfer, version 8.00 (Golden Software Inc., Colorado, USA) was used for the drawing of the Kosovo's map with the distribution of the sample concentration range. The statistical data analysis was achieved by using Stata data analysis and statistical software, version 7.0 (Stata Corporation, Texas, USA).

4. Results and discussion

In Table 1, we present the uranium concentration in the water samples analyzed from four different drinking water sources throughout the territory of Kosovo. 98.8% of the samples analyzed had uranium concentration higher than 0.01 μg L^{-1}. We found a

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