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Short communication

Natural and anthropogenic radioactivity in the environment of Kopaonik mountain, Serbia☆

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A B S T R A C T

To evaluate the state of the environment in Kopaonik, a mountain in Serbia, the activity concentrations of ^{4}K, ^{226}Ra, ^{232}Th and ^{137}Cs in five different types of environmental samples are determined by gamma ray spectrometry, and radiological hazard due to terrestrial radionuclides is calculated. The mean activity concentrations of natural radionuclides in the soil are higher than the global average. However, with an exception of two sampling locations, the external radiation hazard index is below one, implying an insignificant radiation hazard. Apart from ^{40}K, content of the natural radionuclides is predominantly below minimum detectable activities in grass and cow milk, but not in mosses. Although ^{137}Cs is present in the soil, grass, mosses and herbal plants, its specific activity in cow milk is below minimum detectable activity. Amongst the investigated herbal plants, *Vaccinium myrtillus* L. shows accumulating properties, as a high content of ^{137}Cs is detected therein. Therefore, moderation is advised in consuming *Vaccinium myrtillus* L. tea.

1. Introduction

Naturally occurring radionuclides in the environment represent the main source of the radioactivity exposure for humans and biota. Anthropogenic activities affect the distribution of natural radioactivity. Various applications of nuclear energy, coal combustion, production and application of phosphorus fertilizers, mining industry and formation of radioactive waste dumps contribute to redistribution of natural radioactivity. A military operation, undertaken by the North Atlantic Treaty Organization (NATO) against Yugoslavia in 1999, caused environmental contamination with depleted uranium of southern parts of Serbia (UNEP, 2002). During the NATO bombing, Kopaonik, among other locations, was under a heavy and prolonged attack, which resulted in the destruction of the terrain and disruption of the forest ecosystem (UNEP/UNCHS BTF, 1999).

Once in the environment, radioactive material can get incorporated into food as it is taken up by plants or ingested by animals (WHO, 2011). Plants with an ability to accumulate high concentrations of radionuclides have a potential to act as biomonitors and thus help to identify areas of radiation risk. A number of studies have shown that mosses, lichens and mushrooms are typical representatives of bioindicator plants for radionuclides present in the environment (Delfanti et al., 1999; Grdović et al., 2010; Mitrović et al., 2009; Steinnes and Njåstad, 1993; UNSCEAR, 2008). Mosses have some advantages compared to other bioindicator species: their accumulating capacity is higher than of other plants (Elstner et al., 1987); their ability to indicate quality of the air, water and soil, based on their presence, absence or floristic composition, is an important characteristic in facilitating their role as bioindicators of radioactive contamination (Grdović et al., 2010); and mosses entrap airborne particulates, both passively and actively, through an extra cellular ion-exchange (Knight et al., 1961). For these reasons, a comprehensive radioecological study needs to include moss samples.

Since transfer of radionuclides through food chain leads to humans via both plants and animals, our study also encompasses other environmental samples: soil, grass, cow milk and herbal plants. Radioactive contamination of animal feed, such a grass, hay and ensilaged crops, is a major route for animal contamination (Howard et al., 2001). Milk and dairy products are important

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foodstuff in human infant and adult diet, and it is necessary for them to be safe for human consumption. Beside animal products, herbal teas can also contribute to human contamination with radionuclides (Mitrović et al., 2015).

The goal of this paper is to determine the level of radioactivity in different environmental samples from Kopaonik. Apart from the artificial ^{137}Cs (half-life 30 years), three naturally occurring radionuclides: ^{40}K, ^{232}Th and ^{226}Ra are investigated. In addition, an analysis of ^{238}U in the soil is performed.

Caesium-137 is a fission product, and it is a significant indicator of anthropogenic pollution in the environment. Mosses are good bioindicators of this radioisotope (Sawidis et al., 2009). However, it can also be detected in higher plants (Todorović et al., 2013). Radioactive contamination with radiocaesium occurred in Serbia after the 1986 nuclear accident in Chernobyl. A radioecological study, conducted in 1987 (Mićić et al., 1989), showed an increased level of radioactive caesium in the environment of Kopaonik.

Radionuclide ^{40}K (half-life 1.248×10^9 years) is an isotope of potassium that is abundant in nature and is crucial for functioning of all living cells. Natural uranium is a mixture of three radioisotopes: ^{238}U (99%, half-life 4.5×10^9 years), ^{235}U (0.71%), and ^{234}U (0.006%). Its most important daughter is ^{226}Ra (half-life 1602 years), which decays to another important radioactive isotope – radon. Thorium-232 (half-life 1.405×10^{10} years) is less radioactive than uranium, but more abundant in nature. These radionuclides in the soil significantly contribute to the total dose of irradiation to population and environment (Fisenne, 1993).

Hence, in this paper, the radionuclides' contents in the environmental samples are determined, and radiation hazard parameters are calculated to evaluate the state of the environment in Kopaonik. In attempt to assess a long-term impact of pollution events caused by human activities, our results are further compared with the results of two studies performed at the same location: Mićić et al. (1989) conducted a study in 1987, one year after the Chernobyl nuclear accident, and Esposito et al. (2002) investigated an influence of the NATO bombing in 1999.

2. Materials and methods

2.1. Sampling site

Kopaonik is a mountain range in the south western part of the Republic of Serbia. The largest ski resort in Serbia, located around the Kopaonik slopes under the highest peak, Pančićev vrh (elevation 2017 m a.s.l.), and a national park, with its diverse plant and animal species, make Kopaonik a popular tourist destination. The climate of Kopaonik is subalpine and the annual average precipitation rate is up to 1000 mm.

Fig. 1. Sampling locations in Kopaonik, Serbia.

Seven sampling locations were included in this study (Fig. 1): Brus (43.3842 °N 21.0275 °E), Jošanička banja (43.3854 °N 20.7516 °E), Đerekare (43.2586 °N 20.9026 °E), Brzeće (43.2964 °N 20.8809 °E), Lisina (43.2830 °N 20.7400 °E), Gobelja (43.3181 °N 20.8219 °E), and Pančićev vrh (43.2836 °N 20.8110 °E), which represent a subset of the sampling locations in Mićić et al. (1989). This choice of the locations allowed a direct comparison of the activity concentrations obtained in 1987 (Mićić et al., 1989) and 26 years later (this study).

2.2. Sample collection and preparation

Sampling of uncultivated soil, grass, cow milk, moss and herbal plants was conducted during autumn 2013. At each location, five subsamples of the soil, grass, moss and herbal plants were collected randomly, and a composite sample was formed immediately afterwards. Soil samples were collected from a depth of 0–10 cm. Pasture grass was sampled. Stems, leaves, and flowers of six different herbal plants: *Achillea millefolium* L., *Hypericum perforatum* L., *Salvia officinalis* L., *Thymus serpyllum* L., *Teucrium montanum* L., and *Vaccinium myrtillus* L. were gathered. Milk samples, with the composite sample volume of 1 L, were collected at local farms in four sites.

The samples of grass, moss and herbal plants were cleaned from soil and litter, dried in the oven at a temperature of 105 °C until constant weight, and then homogenised and stored in cylindrical containers.

2.3. Activity concentration determination

Activity concentrations of ^{40}K, ^{238}U, ^{226}Ra, ^{232}Th and ^{137}Cs were determined by gamma ray spectrometry on an High Purity Germanium detector (ORTEC), with a relative efficiency of 30% and energy resolution 1.85 keV (1332.5 ^{60}Co). The detector efficiency calibration was performed for different geometries and different matrices, in accordance with the measured sample type.

We used commercially available standards with mixed radionuclides:

- ^{241}Am, ^{133}Ba, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{54}Mn, ^{113}Sn,^{85}Sr, ^{88}Y, dispersed in silicone resin in Marinelli beaker, density (0.98 ± 0.01) g cm^{-3}, volume 1 l; and
- ^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{113}Sn, ^{85}Sr, ^{88}Y, dispersed in silicone resin in Marinelli beaker, density (1.22 ± 0.01) g cm^{-3}, volume 1 l.

The first calibration was used for the cow milk measurements; the second for the soil measurements. The counting time for milk and soil, as well as for background, was 60,000 s.

The system was calibrated for cylindrical geometry using certified reference materials IAEA-330 (spinach) and Moha Barna standard. The counting time for grass, herbal plants and moss, as well as for background, was 250,000 s. The measurements were performed according to a procedure described in our previous works (Mitrović et al., 2009; 2015).

The analysis of each measured gamma ray spectrum was carried out by a software program GAMMA VISION-32. All obtained results are expressed as (mean ± standard deviation).

The analysis of ^{238}U by gamma spectrometry relies on the hypothesis of equilibrium conditions between the parent nuclide ^{238}U and its daughters, ^{234}Th (63.2 keV) and ^{234m}Pa (1001 keV). The ^{226}Ra activity was determined from the gamma line of 186.1 keV corrected for ^{235}U, and ^{226}Ra daughters in equilibrium, ^{214}Bi (609.3, 1120.2 and 1764.5 keV) and ^{214}Pb (351.9 keV). In the case of ^{232}Th, three photo peaks of ^{228}Ac (338, 911.2 and 969 keV) were used in the same way. The activities of ^{40}K and ^{137}Cs were derived from the