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The radiochemical contamination (^{210}Po and ^{238}U) of zone around phosphogypsum waste heap in Wiślinka (northern Poland)

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Abstract. The aim of this work was the determination of the impact of phosphogypsum waste heap in Wiślinka (northern Poland) for radiological protection of zone around waste heap. The activity of ^{210}Po, ^{234}U, and ^{238}U were measured using an alpha spectrometer. The values of uranium and polonium concentration in water with immediate area of waste heap are considerably higher than in the waters of the Martwa Wisła river. The values of activity ratio ^{234}U/^{238}U are approximately about one in the phosphogypsum (0.97±0.05) and in the water of retention reservoir and pumping station (0.92±0.01 and 0.99±0.08), while in the water from the Martwa Wisła river they are slightly higher than one (1.03±0.07 and 1.17±0.06). In the analyzed plants species the highest amounts of polonium and uranium were found in ruderal plants samples as well as hygrophilous plant samples. The more amounts of ^{210}Po and ^{238}U radionuclides were accumulated mainly in the roots of the analyzed plant species. The significant source of polonium and uranium in the natural environment is dry and wet atmospheric fallout in the immediate vicinity of phosphogypsum waste heap and the transfer via root for distant areas. The general conclusion of realized study is higher influence of phosphogypsum on radioactive contamination of environmental zone around heap waste in Wiślinka (northern Poland).

Keywords: polonium, ^{210}Po, uranium, ^{234}U, ^{238}U, water, plants, soils, phosphogypsum waste heap, Wiślinka (northern Poland)

Introduction

One of significant components of the Vistula river delta in northern part of Poland is phosphogypsum waste dump near Wiślinka village. The essence of radiotoxicity of phosphogypsum waste heap is not only gamma radioactivity, but very important are natural alpha radioactive elements, which are leached by rains and bioaccumulated in plant and animal organisms as well as in human organism. In the longer time they can cause the development of cancer disease (Skwarzec, 1995). Uranium is a very dense, highly reactive metallic element that has the highest atomic mass of the naturally occurring elements. The principal source of uranium in the natural environment is the atmospheric precipitation of terrigenic material, as well as river waters and fertilizers. Moreover the concentration of uranium in the natural environment is increased by human activity including industry, fossil fuel combustion, metallurgy, oil refinery, nuclear industry, nuclear weapon tests, the use of uranium ammunition, the manufacture and processing of fuel rods, ore mining, as well as phosphogypsum waste heap (Skwarzec, 1995; Boryło et al., 2012). The main source of ^{210}Po in the environment is ^{210}Pb and ^{210}Po falling to the ground from the atmosphere, small amount of ^{210}Po is formed *in situ* as a result of the radioactive decay of uranium contained in seawater and additional quantities are emitted directly from the Earth as a result of forest fires and volcanic eruptions (Skwarzec, 1995).

Materials and Methods

The surface water samples (10 l) were collected in November, October and December 2007 and 2008 from area around the phosphogypsum waste dump and from the Martwa Wisła river. Down the main current of the Martwa Wisła river samples were collected in Przegalina, Sobieszewko and Górki Wschodnie. The deep water samples (10 l) were collected by piezometer at the depth of 18 m below the surface in July 2009, but phosphogypsum samples were collected in 1997 and 2007. The chosen species plants (ruderal, hygrophilous, edible plants and corn) were collected in 2008 and 2009 (Fig. 1). By comparison the same cultivated plants were collected in Luzino (near Wejherowo city) and Czapielsk (near Kolbudy city). The plants after collection were separated into green parts and root. The method of polonium ^{210}Po and uranium (^{234}U, ^{238}U) determination in analyzed samples was based on procedures established by Skwarzec (1995; 1997; 2009). The activity of ^{210}Po, ^{234}U, and ^{238}U were measured using an alpha spectrometer. Minimum detectable activity (MDA) was calculated as 0.1 mBq for ^{210}Po and 0.3 mBq for ^{238}U. The accuracy and precision of the radiochemical methods were within 10%, based on an international laboratory comparison using International Atomic Energy Agency reference materials (IAEA—384, IAEA—385, IAEA—414). The results of ^{210}Po, ^{234}U, and ^{238}U concentrations in analyzed samples are given with standard deviation (SD) calculated for a 95% confidence interval.

Results and Discussion

The obtained results of polonium and uranium determination in various environmental samples from Wiślinka area are given in Table 1. The phosphogypsum samples are very much enriched in ^{210}Po in comparison to ^{234}U and ^{238}U activity. The contents of ^{210}Po and ^{238}U radionuclides in phosphogypsum are immediately connected with the phosphoric acid production technology and concentration of these radionuclides in phosphorites (Burnett at al., 1996). In the Wiślinka waste heap the estimated activity in 16 mln ton of phosphogypsum contains about 10.5 10^9 Bq for ^{210}Po and 1.6 10^9 Bq for $^{234+238}$U.

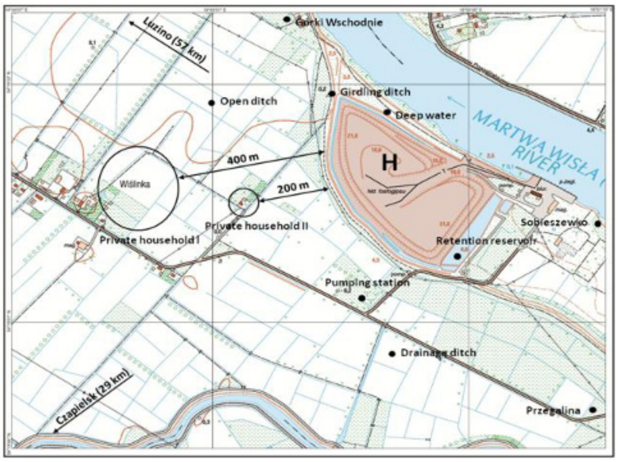

Fig.1 The sites of environmental samples collected (H – phosphogypsum waste heap; I, II–private household)

The highest concentrations of ^{210}Po and ^{238}U isotopes were observed in water samples from Wiślinka area: in pumping station and retention reservoir (166±1 mBq dm^{-3} and 14430±69 mBq dm^{-3}, respectively) which contains only contaminants from phosphogypsum waste heap (Tab. 1, Fig. 2). This fact can be explained by the lixiviation of polonium and uranium from phosphogypsum waste dump to water. Polonium and uranium concentration in the bottom water of the analyzed retention reservoir and pumping station increases with depth, indicating the diffusion process from dump surface to water. The relatively lower uranium and polonium concentrations were observed in water samples taken along the Martwa Wisła river. The values of the activity ratio ^{234}U/^{238}U in waters from the Martwa Wisła river ranged from 1.03±0.07 to 1.17±0.06 and are lower than characteristic values for fresh water of precipitation origin (Table 1). The results obtained so far show that the migration and distribution of uranium and polonium from the phosphogypsum waste heap to the Martwa Wisła river are rather slow. The values of the activity ratio ^{234}U/^{238}U in water samples collected in the immediate vicinity of phosphogypsum waste heap ranged from 0.92±0.01 to 0.99±0.08 which is consistent with phosphogypsum origin of polonium and uranium isotopes. The maximum limit of permissible alpha and beta emitters in drinking water (generally: ^{210}Po, ^{226}Ra, ^{234}U, ^{238}U) is 0.1 Bq dm^{-3} according to WHO (WHO, 1996). The obtained results can certify about potential hazard for humans and grazing animals in Wiślinka waste area because significant amount only 3 radionuclides (^{210}Po, ^{234}U, ^{238}U) exceeds 0.1 Bq l border.

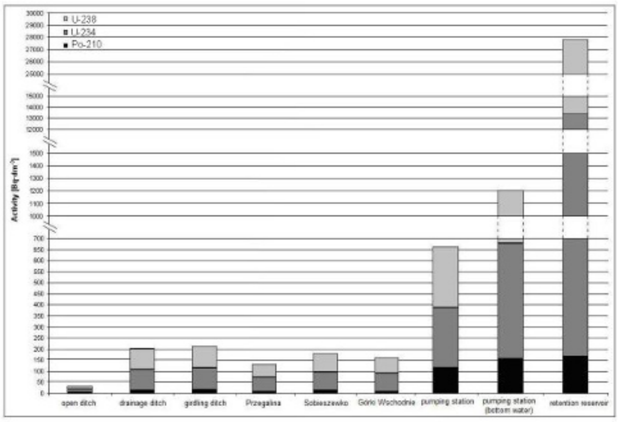

Fig.2 The ^{210}Po, ^{234}U and ^{238}U activity in water samples collected in November, October and December 2007 and 2008 near phosphogypsum waste heap area in Wiślinka and along the Martwa Wisła river

Among analyzed plants the highest concentrations of ^{210}Po, and ^{238}U were noticed for ruderal plants. Moreover the higher ^{210}Po, and ^{238}U concentrations were measured in roots, but the lower in green parts of plants. The values of the activity ratio ^{234}U/^{238}U in analyzed plants ranged from 0.96±0.06 to 0.97±0.12 for ruderal plants and from 0.98±0.06 to 0.99±0.04 for hygrophilous plants and indicate that uranium in analyzed plants originates from the phosphogypsum waste heap (Tab. 1). It is particularly important that the highest ^{210}Po and ^{238}U concentrations were characterized for ruderal plants, which are covered with tomentose hairs. The higher activity of polonium and uranium in hygrophilous plants suggests that groundwater is a very important source of radionuclides to tissues and organs of these plants. The ratios of ^{234}U/^{238}U in analyzed hygrophilous plants were near one, which is consistent with their phosphogypsum character and are similar to values for water from the retention reservoir. The smaller ^{210}Po and ^{238}U concentrations were noticed in edible plants. However, only in this group of plants the highest polonium and uranium concentrations were measured in green parts of the analyzed plants (Tab. 1). As for the meadow, hygrophilous and ruderal plants the larger, pinnate and undulating surface of leaves of analyzed plants are convenient place of polonium and uranium deposition. This structure probably can retain phosphogypsum dust. The maximum ^{210}Po and ^{238}U concentrations were measured in old leaves and those longer exposed to atmospheric fallout. It is suggested that the transfer of the analyzed radionuclides via the root system is rather negligible. The principal sources of polonium and uranium in analyzed edible plants are dry atmospheric fallout and precipitation, and soil resuspension process. The smaller concentrations of ^{210}Po and ^{238}U were observed in roots of analyzed edible plants (Tab. 1). Despite having the same storage root system and the same tubers, plants accumulate varied amounts of radionuclides and this fact may be connected with e.g. turgidity of plants (determined by the water saturation) (Boryło and Skwarzec, 2011). Also the some herbaceous perennial flowering plants have a very shortened stem, which forms the so-called 'bulb' (Szafer et al., 1988). Thanks to this structure the water from atmospheric precipitation can flow downwards to the underground part of plant (Boryło and Skwarzec, 2011).

The values of activity ratio ^{234}U/^{238}U are between 0.92±0.05 and 0.99±0.08 for edible vegetables, which were collected from private household II and from 0.96±0.10 to 0.99±0.09 for corn (private household I) (Tab. 1). It is a typical feature of the phosphoric rocks used for fertilizer production (Roselli et al., 2009) or typical for phosphogypsum samples. The ^{210}Po and ^{238}U concentrations in crop plants from phosphogypsum waste heap recorded in this study are generally higher than in control sites (Fig. 3).

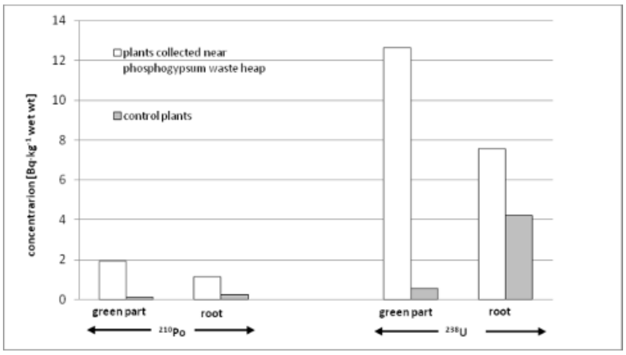

Fig.3 The comparison of ^{210}Po and ^{238}U concentration in edible plants, which were collected in the vicinity of phosphogypsum waste heap and control edible plants

The activity ratio ^{234}U/^{238}U in analyzed edible control plants is 1.02±0.09 (Tab. 1). On the basis of values of ^{210}Po and ^{238}U concentrations in edible plants from phosphogypsum waste zone and uncontaminated area from Czapielsk and Luzino, it was calculated that radiochemical contaminations of vegetables from private household are respectively 22 and 4 for ^{210}Po in green parts and roots as well as 6.4 and 3 for ^{238}U in green parts and roots times higher in comparison to non-contaminated vegetables (control samples). The substratum soil for analyzed plants were two types of soil: alluvial soils (generally private household I and II near phosphogypsum waste heap and private household near Czapielsk and Luzino) and peat (area near phosphogypsum waste heap).

The radionuclides activities in soil samples, which were collected around and from the slope of phosphogypsum waste heap, were much higher: from 23±1 to 150±3 Bq kg^{-1} wet wt for ^{210}Po and from 87±5 to 342±11 Bq kg^{-1} wet wt for ^{238}U. The lower polonium and uranium radionuclides' activities were estimated for soil samples from private household (alluvial soil) (Tab. 1).

Conclusion

As a result of resuspention from the surface of phosphogypsum waste heap aerosols are emitted to immediate surroundings. Apart from atmospheric deposition, the plants can receive radionuclides from radioactive fallout and from the phosphogypsum fertilized soils. The obtained results of determinations of radionuclides in various environmental points indicate that the 300-meter buffer zone is not able to offset the negative influence of phosphogypsum waste heap on the surrounding environment.

Acknowledgments

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Tab.1 The average ^{210}Po and ^{238}U concentration and values of the activity ^{234}U/^{238}U ratio in analyzed samples

Samples	^{210}Po	^{238}U	Total uranium	Activity ratio ^{234}U/^{238}U
	water [mBq dm^{-3}] soil, plants and phosphogypsum [Bq kg^{-1} w. wt.]		[µg dm^{-3}] [mg kg^{-1}]	
1. Phosphogypsum	654 ± 11	28.1 ± 0.8	2.29 ± 0.07	0.97 ± 0.05
2. Water around waste heap				
Retention reservoir	166 ± 1	14430 ± 69	1177 ± 6	0.92 ± 0.01
Pumping station (bottom water)	155 ± 3	527 ± 28	43 ± 2	0.99 ± 0.08
Pumping station	115 ± 6	275 ± 72	22 ± 1	0.99±.0.05
Drainage ditch	15 ± 1	96 ± 12	7.8 ± 0.1	1.03 ± 0.05
Girdling ditch	13 ± 1	91 ± 11	7.4 ± 0.1	1.02 ± 0.05
Open ditch	4.0 ± 0.1	13.0 ± 0.1	1.1 ± 0.1	1.15 ± 0.05
Deep water	21.4 ± 1.7	151 ± 2	12 ± 1	0.98 ± 0.05
3. Water (Martwa Wisła river)				
Przegalina	7 ± 1	60 ± 3	4.9 ± 0.2	1.08 ± 0.05
Sobieszewsko	12 ± 2	82 ± 4	6.7 ± 0.4	1.03 ± 0.07
Górki Wschodnie	8 ± 1	71 ± 3	5.8 ± 0.2	1.17 ± 0.06
4. Soil				
Area near waste heap	23 ± 1	87 ± 5	7.1 ± 0.4	1.01 ± 0.08
Area near retetion reservoir	148 ± 7	69 ± 7	5.6 ± 0.1	0.98 ± 0.06
Slope of waste heap	150 ± 3	342 ± 11	28 ± 1	1.00 ± 0.05
Private household II	19.1 ± 0.1	168 ± 5	13.7 ± 0.5	1.00 ± 0.05
Private household I	16 ± 1	115 ± 5	9.4 ± 0.3	1.00 ± 0.05
Private household (control soil)	4.1 ± 0.1	56 ± 2	5 ± 2	1.04 ± 0.06
5. Plants				
Meadow plants				
• green parts	5.6 ± 0.1	5.5 ± 0.4	0.40 ± 0.03	0.98 ± 0.07
• roots	11.3 ± 0.1	7.1 ± 0.3	0.58 ± 0.03	0.99 ± 0.06
Hygrophilous plants				
• green parts	18 ± 1	42 ± 2	3.4 ± 0.2	0.98 ± 0.06
• roots	84 ± 3	130 ± 4	5.5 ± 0.2	0.99 ± 0.04
Ruderal plants				
• green parts	51 ± 1	36 ± 3	3.0 ± 0.2	0.97 ± 0.12
• roots	89 1	68 ± 3	5.5 ± 0,3	0.96 ± 0.06
Corn				
• green parts	2.1 ± 0.1	3.0 ± 0.2	0.25 ± 0.02	0.96 ± 0.10
• roots	6.4 ± 0.3	5.5 ± 0.4	0.45 ± 0.03	0.99 ± 0.09
Edible plants				
• green parts	2.2 ± 0.1	10.8 ± 0.4	0.88 ± 0.04	0.92 ± 0.05
• roots	1.2 ± 0.1	8 ± 1	0.65 ± 0.04	0.99 ± 0.08
Edible plants (control plants)				
• green parts	0.1 ± 0.1	1.7 ± 0.1	0.14 ± 0.04	1.02 ± 0.09
• roots	0.30 ± 0.02	2.7 ± 0.1	0.22 ± 0.01	1.02 ± 0.08