NUKLEONIKA 2010;55(2):187–193

ORIGINAL PAPER

Polonium (^{210}Po) and uranium (^{234}U, ^{238}U) in water, phosphogypsum and their bioaccumulation in plants around phosphogypsum waste heap at Wiślinka (northern Poland)

Bogdan Skwarzec, Alicja Boryło, Alicja Kosińska, Sylwia Radzajewska

Abstract. The principal sources of polonium and uranium radionuclides the Wiślinka area waste dump are phosphorites and phosphogypsum produced by the Phosphoric Fertilizers Industry of Gdańsk. The values of uranium and polonium concentration in water with immediate surroundings of waste heap are considerably higher than in the waters of the Martwa Wisła river. The activity ratio $^{234}U/^{238}U$ is approximately about one in the phosphogypsum (0.97±0.06 and 0.99±0.04) and in the water of a retention reservoir and a pumping station (0.92±0.01 and 0.99±0.04), while in the water from the Martwa Wisła river is slightly higher than one (1.00±0.07 and 1.06±0.02). The leaching process of uranium and polonium from the phosphogypsum waste heap is responsible for the maximum uranium concentration (1097±6 μg·dm^{-3} and 1177±6 μg·dm^{-3}) and the high ^{210}Po concentration (131.4±0.9 mBq·dm^{-3} and 165.7±1.4 mBq·dm^{-3}) in the retention reservoir. The major source of polonium and uranium in plants are wet and dry atmospheric falls gathering soil and air dust from the phosphogypsum waste dump and root system. The highest uranium and polonium concentrations were found in older part of grasses (yellow oatgrass, meadow foxtail, moneywort), exposed to atmospheric falls for a long time. The maximum concentrations of ^{210}Po were characterized for samples of plant root collected at the retention reservoir (150.50±4.97 and 108.55±3.95 Bq·kg^{-1} dry mass). Polonium and uranium concentrations in water samples of the Martwa Wisła river are relatively low in comparison with the value in the retention reservoir and pumping station near the phosphogypsum waste heap. This suggests that the radionuclides could be leached from the dumping site to the surrounding environment.

Key words: polonium • uranium • phosphogypsum • plants • water • Wiślinka

Introduction

The phosphogypsum waste heap at Wiślinka is permanently integrated into the landscape of Żuławy Gdańskie (northern Poland). This continuously is raising a great deal of doubts. One of them concerns a plant of the Phosphoric Fertilizers Industry of Gdańsk, the others ecological organizations and local population. The local people are concerned and worried about the idea of refusal to build an incinerator at the Wiślinka village, initiated by the municipal authority. In addition, the process wastes from a thermoelectric power station "Gdańsk" are deposited on the Sobieszewska Island, too.

According to the decision of voivodeship national council (GW-II-0531/115/67) in Gdańsk, the phosphogypsum waste heap came into existence on 27 December 1967. The phosphorites – a main component for the production – are transported to Gdańsk by the Phosphoric Fertilizers Industry from North Africa (Morocco) [15]. Sulphuric acid – the next component – is used for degradation of phosphorites and production of enriched superphosphate (hydrated calcium sulphate). Phosphoric acid, a material for the production

B. Skwarzec, A. Boryło✉, A. Kosińska, S. Radzajewska
Faculty of Chemistry,
University of Gdańsk,
18/19 Sobieskiego Str., 80-952 Gdańsk, Poland,
Tel.: +48 58 523 5338, Fax: +48 58 523 5472,
E-mail: aborylo@chem.univ.gda.pl

Received: 13 July 2009
Accepted: 30 November 2009

of phosphate fertilizers, is obtained in a wet process by the reaction of phosphatic rocks with sulphuric acid [14]. During this process, phosphogypsum is produced which is transported by cargo boats from the Phosphoric Fertilizers Industry of Gdańsk to a waste dump at Wiślinka. Biological reclamation actions are now in progress. Closing down of the Wiślinka waste dump is planned at the end of 2009.

Uranium is spread in nature, occurring in over 160 minerals, locally in high concentrations (between 50–90% uranium content, e.g. uranite, broegerite, becquerelite, cleveite, autunite, carnotite, pitchblende, kasolite) [11, 36]. Higher uranium concentrations are observed, for example, around phosphogypsum stacks [6, 18, 20, 27]. The principal source of uranium in the natural environment is atmospheric precipitation of terrigenic material, as well as river waters and fertilizers [33]. In addition, the concentration of uranium in the natural environment is increased by results of human activity – industry, fossil fuel combustion, phosphate fertilizers in agriculture, domestic and industrial sewage [30]. Natural uranium consists of three alpha radioactive isotopes: 99.2745% of ^{238}U, 0.7200% of ^{235}U and 0.0054% of ^{234}U [4, 8]. 1 Bq ^{238}U corresponds to 81.6 μg of natural uranium (1 μg of natural U – 12.3 mBq of ^{238}U) [26]. The ^{234}U isotope belongs to the natural radioactive decay series of ^{238}U [21]. The specific radioactivity of natural uranium (^{234}U, ^{235}U and ^{238}U) is about 25,446 Bq·g^{-1} [4, 20], although the specific radioactivity of ^{238}U is lower (1.24×10^4 Bq·g^{-1}) in comparison with ^{234}U (2.30×10^8 Bq·g^{-1}) [9].

The ^{234}U and ^{238}U radionuclides are not in the radioactive state of equilibrium in the natural environment, higher disequilibrium has been noticed in seawater rather than in sediments [30, 34]. In the southern Baltic (Gulf of Gdańsk) waters the mean value of ^{234}U/^{238}U activity ratio was found to be 1.17, while in the sediments it is about 1.00 [30, 35]. In the aquatic environment uranium exists in the two valency states: U(IV) and U(VI). In oxidated form in sea and river water there are soluble carbonate complexes: $[UO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_2]^{2-}$ [30].

The uranium is a radioactive and toxic metal, it is a hazardous environmental pollutant. It is relatively highly toxic to humans, both chemically and radiologically (its progeny are highly radioactive). The compounds of uranium can penetrate the blood from alveoli pockets in the lungs or through the gastrointestinal (GI) tract as a result of consumption of contaminated water or food. The residence time of the insoluble uranium in the GI tract is estimated in years. Due to its heavy metal nature, the presence of uranium in the body causes damage to the kidney leading to nephritis. The limit of permissible uranium in drinking water is 30 μg·dm^{-3} according to the United States Environmental Protection Agency [12] and 15 μg·dm^{-3} according to the World Health Organization (WHO) [38].

Polonium ^{210}Po, belongs to the natural uranium decay series starting from ^{238}U, but its fate depends on the further members of this series, e.g. ^{226}Ra and most of all on ^{210}Pb. ^{222}Rn escaping from the earth's surface constitutes the source of atmospheric ^{210}Po [31]. The main source of ^{210}Po in environmental pollution is ^{210}Pb and ^{210}Po falling to the ground with atmosphere. A small amount of ^{210}Po is formed *in situ* as a result of the radioactive decay of uranium contained in seawater. Apart from ^{210}Po formed by the decay of ^{210}Pb contained in the air, its additional quantities are emitted directly from the earth as a result of forest fires and volcanic eruptions [31]. The specific radioactivity of polonium ^{210}Po is very high and equals 1.66×10^{14} Bq·g^{-1}, and its half-life is 138.4 days [9]. Polonium ^{210}Po belongs to the most radiotoxic nuclides to human beings [33]. The limit of all permissible alpha emitters in drinking water is 0.1 Bq·dm^{-3} according to the World Health Organization (WHO) [38].

The objective of this study was the determination of uranium and polonium concentration in surface and bottom water samples, phosphogypsum and some plants from the area around the phosphogypsum waste dump and from the Martwa Wisła river in northern part of Poland.

Experimental

The surface water samples (10 dm^{-3}) were collected in October and December 2008 from the area around the phosphogypsum waste dump at Wiślinka and from the Martwa Wisła river. Down the main current of the Martwa Wisła river samples were collected at Przegalina, Sobieszewko and Górki Wschodnie. The places of the surface water, phosphogypsum and plant sampling (yellow oatgrass, meadow foxtail, moneywort) are presented in Fig. 1. Phosphogypsum and plant samples were collected in December 2008 and February 2009.

The radiochemical method for polonium ^{210}Po and uranium (^{234}U, ^{238}U) determination in analyzed samples was based on the procedure established by Skwarzec [30–32].

Radioactivity of ^{210}Po, ^{234}U and ^{238}U was measured using alpha spectrometry equipment with semiconductor silicon detectors of 300 mm^2 active surface barrier (Canberra-Packard, USA). Polonium samples were measured for 2–3 days and their radioactivity was calculated on the electrodeposition day. Uranium samples were measured for 3–5 days. The polonium and uranium yield in the analyzed samples ranged from 50 to 80%. The results of ^{210}Po, ^{234}U and ^{238}U concentration in the analyzed samples are given with standard deviation (SD) calculated for 95% confidence intervals. The trueness and precision of the radiochemical methods were evaluated using International Atomic Energy Agency (IAEA) reference materials (IAEA-384, IAEA-385, IAEA-414), estimating that the absolute relative bias is less than 10%.

Results and discussion

The results of ^{234}U and ^{238}U measurements in surface water samples are given in Tables 1, 2 and Fig. 2. The highest concentrations of uranium isotopes and total uranium in samples collected in October and December 2008 were observed in water from the pumping station and retention reservoir of the phosphogypsum waste heap at Wiślinka. A higher uranium concentration was confirmed in the pumping station (from 250 ± 7 mBq·dm^{-3} to 275 ± 7 mBq·dm^{-3} for ^{238}U and from 248 ± 7 mBq·dm^{-3} to 273 ± 7 mBq·dm^{-3} for ^{234}U in the

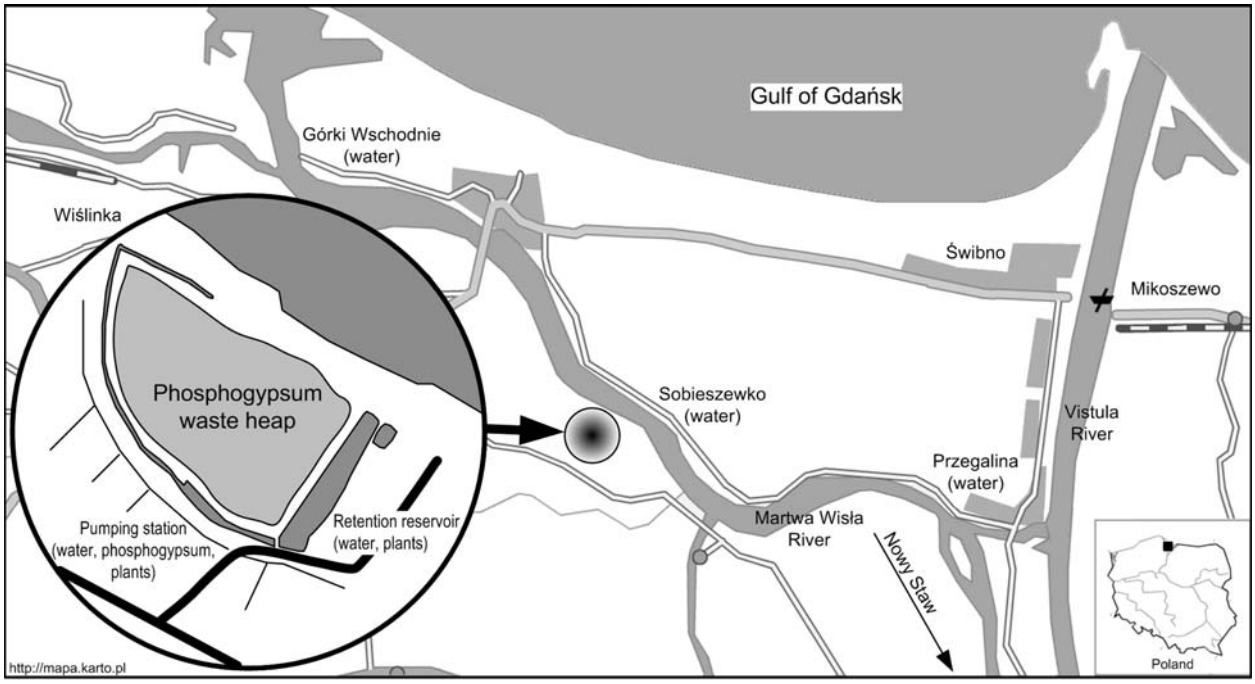

Fig. 1. Place of taking water, phosphogypsum, plant samples (October and December 2008, February 2009).

surface water and from 507±28 mBq·dm^{-3} to 527±28 mBq·dm^{-3} for ^{238}U and from 498±27 mBq·dm^{-3} to 524±28 mBq·dm^{-3} for ^{234}U in the bottom water), the highest uranium amounts, thousand times higher than those observed in the Martwa Wisła river, were found in the retention reservoir (13.440±68 mBq·dm^{-3} and 14.430±69 mBq·dm^{-3} for ^{238}U, 13.140±65 mBq·dm^{-3} and 13.240±66 mBq·dm^{-3} for ^{234}U). Consumption of this water by wild animals could be dangerous because the preliminary radiological criterion for drinking water is gross alpha radioactivity 0.1 Bq·dm^{-3} or gross beta radioactivity 0.1 Bq·dm^{-3} [22]. The enriched amounts of uranium and thorium radionuclides have been measured in water and suspended matter samples in the estuarine system of the Odel river (Spain) near the fertilizer processing complex [23, 24]. The obtained results confirm hypothesis that uranium is leached from phosphogypsum waste dump to surface and bottom water of the retention reservoir. Uranium concentration in the bottom water of the analyzed retention reservoir and pumping station ditch increases with depth, indicating the diffusion process from dump surface to water. The average values of the ^{234}U/^{238}U activity ratio in the analyzed pumping station and retention reservoir oscillated between 0.92–0.99. These data indicate that the general source of uranium is phosphogypsum. Also the uranium concentration in groundwaters around the fertilizer factory complex in Spain was considerably higher than those in other areas of the same aquifer [1]. The potential leaching of radionuclides from sedimen-

Table 1. The uranium concentration and values of the ^{234}U/^{238}U activity ratio in water samples from the phosphogypsum waste heap and Martwa Wisła river in October 2008

Sampling location	^{238}U (mBq·dm^{-3})	^{234}U (mBq·dm^{-3})	Total uranium (μg·dm^{-3})	Activity ratio ^{234}U/^{238}U
Przegalina	25.34 ± 0.99	25.38 ± 0.99	2.07 ± 0.08	1.00 ± 0.06
Sobieszewko	33.63 ± 1.61	32.55 ± 1.65	2.82 ± 0.13	1.06 ± 0.02
Górki Wschodnie	30.34 ± 0.94	31.38 ± 0.98	2.47 ± 0.08	1.03 ± 0.04
Pumping station – surface water	250 ± 7	248 ± 7	20.41 ± 0.57	0.99 ± 0.04
Pumping station – bottom water	507 ± 28	498 ± 27	41.36 ± 2.13	0.98 ± 0.07
Retention reservoir	13.440 ± 68	13.140 ± 65	1097 ± 6	0.97 ± 0.07

Table 2. The uranium concentration and values of the ^{234}U/^{238}U activity ratio in water samples from the phosphogypsum waste heap and Martwa Wisła river in December 2008

Sampling location	^{238}U (mBq·dm^{-3})	^{234}U (mBq·dm^{-3})	Total uranium (μg·dm^{-3})	Activity ratio ^{234}U/^{238}U
Przegalina	60.23 ± 2.61	62.26 ± 2.65	4.91 ± 0.21	1.03 ± 0.06
Sobieszewko	82.39 ± 4.32	82.62 ± 4.32	6.72 ± 0.35	1.00 ± 0.07
Górki Wschodnie	70.52 ± 3.01	72.31 ± 3.21	5.75 ± 0.24	1.02 ± 0.06
Pumping station – surface water	275 ± 7	273 ± 7	22.45 ± 0.56	0.99 ± 0.05
Pumping station – bottom water	527 ± 28	524 ± 28	42.99 ± 2.31	0.99 ± 0.08
Retention reservoir	14.430 ± 69	13.240 ± 66	1177 ± 6	0.92 ± 0.01

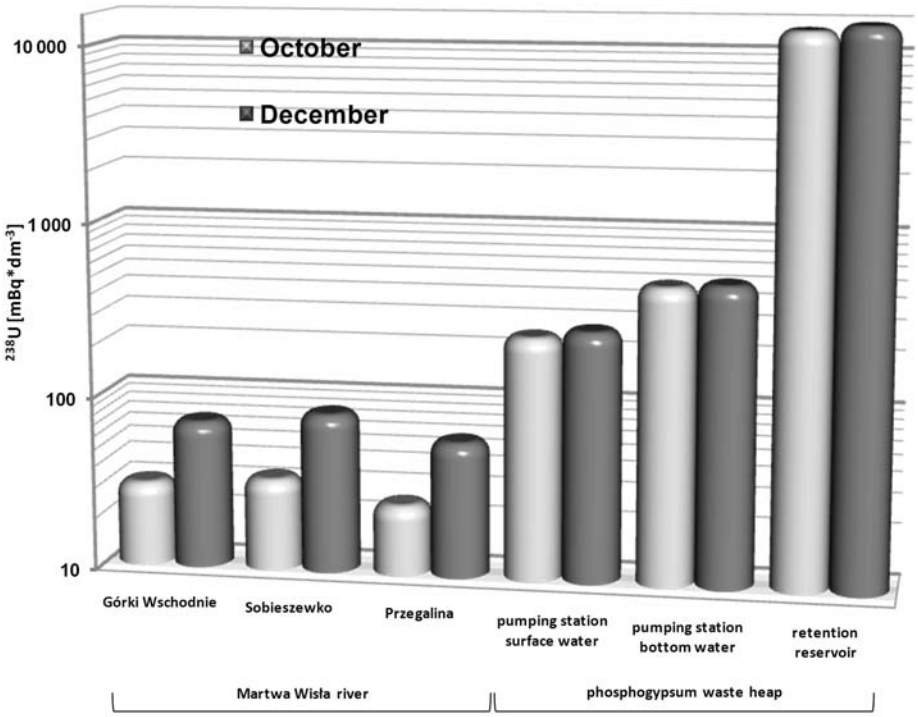

Fig. 2. ^{238}U radioactivity in water samples collected in October and December 2008 from the Martwa Wisła river to the phosphogypsum waste heap at Wiślinka.

tary phosphate rock during the industrial production of phosphoric acid is still studied and discussed [2, 3].

The relatively lower uranium and polonium concentration was observed in water samples taken in October and December 2008 along the Martwa Wisła river. The comparable ^{238}U radioactivity was found at Przegalina and Górki Wschodnie from 25.34±0.99 mBq·dm^{-3} to 60.23±2.61 mBq·dm^{-3} and from 30.34±0.94 mBq·dm^{-3} to 70.52±3.01 mBq·dm^{-3}, respectively. A slightly higher ^{238}U concentration was reported between 33.63±1.61 mBq·dm^{-3} and 82.39±4.32 mBq·dm^{-3} in Sobieszewko (Tables 1, 2 and Fig. 2). The ^{210}Po concentration in the water samples varied from 7.08±0.52 mBq·dm^{-3} (Przegalina) to 7.89±0.50 mBq·dm^{-3} (Górki Wschodnie), and similarly like uranium, a bit higher in Sobieszewko (12.26±2.20 mBq·dm^{-3}) (Table 3). Sobieszewko is located opposite the phosphogypsum waste dump and rainfall waters can be stored and washed from here. The values of the activity ratio in water samples ranged from 1.00 to 1.06 and are characteristic of river waters. Similar values were observed in the Wisła river. The ^{210}Po concentration in Wisła river water samples collected at Kiezmark (20 km from Wiślinka) ranges from 1.88±0.04 mBq·dm^{-3} (in autumn) to 3.49±0.03 mBq·dm^{-3} (in spring). However, uranium total concentrations were estimated at 0.77±0.27 μg·dm^{-3} in winter and 0.52±0.22 μg·dm^{-3} in summer [16]. The results obtained so far show that the migration and distribution of uranium and polonium radionuclides from the phosphogypsum waste heap to the Martwa Wisła river is rather slow.

Table 3. Average polonium ^{210}Po concentration in water samples from the phosphogypsum waste heap and Martwa Wisła river in October 2008

Sampling location	^{210}Po (mBq·dm^{-3})
Przegalina	7.08 ± 0.52
Sobieszewko	12.26 ± 2.20
Górki Wschodnie	7.89 ± 0.50
Pumping station – surface water	114.8 ± 5.8
Pumping station – bottom water	155.1 ± 3.2
Retention reservoir – surface water	131.4 ± 0.9
Retention reservoir – bottom water	165.7 ± 1.4

The content of polonium in water sample from the phosphogypsum waste heap is very diversified. The ^{210}Po concentration ranged from 114.8±5.8 mBq·dm^{-3} to 131.4±0.9 mBq·dm^{-3} and from 155.1±3.2 mBq·dm^{-3} to 165.7±1.4 mBq·dm^{-3} in the surface water of pumping station and the bottom water of retention reservoir (Table 3). The different values of polonium concentration in surface and bottom waters from the pumping station and the retention reservoir showed that the source of radionuclides is the sedimentation and sinking to the bottom layers.

The phosphogypsum samples from the Wiślinka area are very much enriched with natural polonium, ^{210}Po, while the uranium radionuclides (^{234}U and ^{238}U) tend to be in waters around the waste dump. The ^{210}Po concentration in dry samples equals 121.1±4.5 Bq·kg^{-1}, whereas the value in wet phoshpogypsum was calculated as 95.9±5.8 Bq·kg^{-1} (Table 4). The phosphogypsum

Table 4. Average polonium ^{210}Po and uranium concentration and values of the $^{234}U/^{238}U$ activity ratio in phosphogypsum samples

Samples	^{210}Po (Bq·kg^{-1})	^{234}U (Bq·kg^{-1})	^{238}U (Bq·kg^{-1})	Total uranium (mg·kg^{-1})	Activity ratio $^{234}U/^{238}U$
Dry phosphogypsum	121.1 ± 4.5	52.52 ± 1.72	52.08 ± 1.71	4.29 ± 0.14	0.99 ± 0.04
Wet phosphogypsum	95.9 ± 5.8	33.35 ± 1.39	32.37 ± 1.37	2.72 ± 0.11	0.97 ± 0.06

Table 5. Average polonium ^{210}Po and uranium concentration and values of the ^{234}U/^{238}U activity ratio in yellow oatgrass (*Trisetum flavescens Pers.*) samples in December 2008

Trisetum flavescens Pers.	^{210}Po (Bq·kg^{-1})	^{234}U (Bq·kg^{-1})	^{238}U (Bq·kg^{-1})	Total uranium (mg·kg^{-1})	Activity ratio ^{234}U/^{238}U
			Area around retention reservoir		
Near-ground part	52.18 ± 1.56	225.20 ± 6.78	226.41 ± 7.08	18.48 ± 0.58	0.99 ± 0.04
Above ground parts	13.52 ± 0.95	7.46 ± 0.40	7.52 ± 0.40	0.61 ± 0.03	0.99 ± 0.08
			Area around pumping station		
Near-ground part	31.68 ± 2.15	136.39 ± 5.99	140.05 ± 6.07	11.43 ± 0.49	0.98 ± 0.06
Above ground parts	7.87 ± 0.64	6.37 ± 0.38	6.59 ± 0.38	0.54 ± 0.03	0.97 ± 0.08

samples were collected at the foot of the escarpment. The higher ^{210}Po polonium concentration was evaluated in phosphogypsum samples from the escarpment collected in 1997 and 2007, immediately after the acid production (between 613±13 and 695±9 Bq·kg^{-1}) [7]. The chemical behaviour of polonium, ^{210}Po, in phosphogypsum is not understood to be fully explained and requires advanced investigations [14, 25, 37]. Moreover, teams of scientists claimed that ^{210}Po is more mobile in the presence of sulphide ions which could be formed by a bacterial process of phosphogypsum [11, 37]. These high levels of ^{210}Po are explained by a strong building of ^{210}Po in phosphogypsum particles [14].

Uranium isotopes form highly soluble compounds with phosphate ions [28]. The activities of ^{238}U and ^{234}U in phosphogypsum ranged from 32.37±1.37 Bq·kg^{-1} to 52.08±1.71 Bq·kg^{-1} and from 33.35±1.39 Bq·kg^{-1} to 52.52±1.72 Bq·kg^{-1}, respectively (Table 4). The lowest uranium concentrations in phosphogypsum should be a sign that these radionuclides migrate predominantly to phosphoric acid. On the other hand, the concentration of uranium radionuclides in phosphorites and phosphogypsum lay in a very wide range. The radioactivity concentration of ^{238}U in phosphate rock was 638±153 Bq·kg^{-1}, while in phosphogypsum from a factory of Brazilian fertilizers was only 18±3 Bq·kg^{-1}. In other Brazilian factories the highest ^{238}U radioactivity was found in phosphate rocks: 344±94 Bq·kg^{-1} and 14±6 Bq·kg^{-1}, the lowest in phosphogypsum: 61±7 Bq·kg^{-1} and 2±8.97 Bq·kg^{-1}, respectively [28]. The nuclides of uranium ^{234}U and ^{238}U were in the radioactive state of equilibrium in analyzed samples, because the values of the ^{234}U/^{238}U oscillate around one (0.97±0.06 and 0.99±0.04). The research confirmed that the majority of uranium is incorporated into the phosphoric acid, whereas the polonium into the phosphogypsum [13]. For instance, the ^{210}Po concentration in Syrian phosphogypsum varies between 373 and 589 Bq·kg^{-1} [2], in Brazilian phosphogypsum ^{210}Po concentration ranged from 281±27 Bq·kg^{-1} to 673±24 Bq·kg^{-1}, but the whole total uranium ranged from 66±24 Bq·kg^{-1} to 140±22 Bq·kg^{-1} [29].

The flow of radionuclides from the dump surface into the water and soils in immediate surroundings has an impact on contamination level of the natural environment. A higher assimilation power of polonium and uranium was observed in the near-ground part of grasses collected around the area of pumping station and retention reservoir in December 2008 and February 2009 (Table 5). The highest phytovailability of polonium was characterized for yellow oatgrass (*Trisetum flavescens Pers.*). The uranium and polonium concentration in the near-ground parts was higher than in the above ground plant parts. We can afford to formulate thesis that the principal sources of polonium and uranium are dry and wet atmospheric fallouts. The polonium content of atmospheric origin depends on the age of leaves and their surface area. The lower polonium and uranium concentration (between 7.87±0.64 Bq·kg^{-1} and 13.52±0.95 Bq·kg^{-1} for ^{210}Po, between 6.37±0.38 Bq·kg^{-1} and 7.46±0.40 Bq·kg^{-1} for ^{234}U, 6.59±0.38 Bq·kg^{-1} and 7.52±0.40 Bq·kg^{-1} for ^{238}U, as well as between 0.54±0.03 Bq·kg^{-1} and 0.61±0.03 mg·kg^{-1} for total uranium) was measured in young, narrow leaves (Table 5). A higher radionuclide concentration was noticed in old leaves and those longer exposed to atmospheric fall (between 31.68±2.15 Bq·kg^{-1} and 52.18±1.56 Bq·kg^{-1} for ^{210}Po, between 136.39±5.99 Bq·kg^{-1} and 225.20±6.78 Bq·kg^{-1} for ^{234}U, 140.05±6.07 Bq·kg^{-1} and 226.41±7.08 Bq·kg^{-1} for ^{238}U, and between 11.43±0.49 mg·kg^{-1} and 18.48±0.58 mg·kg^{-1} for total uranium) (Table 5). For comparison, the same plant species were collected from Żuławy Wiślane (25 kilometers from the phoshogypsum waste heap, near the city of Nowy Staw). The radionuclides concentrations in this grass amount to 0.29±0.02 Bq·kg^{-1} for ^{210}Po, 0.59±0.03 Bq·kg^{-1} for ^{234}U, 0.49±0.02 Bq·kg^{-1} for ^{238}U in the near-ground part and 0.31±0.03 Bq·kg^{-1} for ^{210}Po, 0.61±0.04 Bq·kg^{-1} for ^{234}U, 0.50±0.03 Bq·kg^{-1} for ^{238}U in the above ground plant part. The value of the ^{234}U/^{238}U activity ratio in Żuławy Wiślane grass is 1.20±0.09 and 1.22±0.09 for the near-ground part and the above ground part, respectively. This is very typical of plants, where the variations are between 1.02 and 1.30 [5, 30]. Values of the ^{234}U/^{238}U activity ratio in yellow oatgrass (*Trisetum flavescens Pers.*) around the phosphogypsum waste heap are near one (0.97±0.08 – 0.99±0.04), which proves explicitly their phosphogypsum character.

The highest polonium concentration was found in the root of meadow foxtail (*Alopecurus pratensis*) and moneywort (*Lysimachia nummularia*) (Table 6). The root system has a significant role in bioaccumulation of radionuclides. Data obtained for polonium content were compared for the pumping station and the retention reservoir areas. The values are about 37.99±2.52 Bq·kg^{-1} and 37.44±1.09 Bq·kg^{-1} dry mass. The maximum polonium concentrations were characterized for samples of grasses located at the retention reservoir (150.50±4.97 and 108.55±3.95 Bq·kg^{-1} dry mass) (Table 6). This can be related to the fact that solum and soil-water substratum of this place is enriched with phosphogypsum. The plants take up polonium

Table 6. Average polonium ^{210}Po concentration in foxtail (*Alopecurus pratensis*) and moneywort (*Lysimachia nummularia*) samples collected from the area phosphogypsum waste heap in February 2009

Samples	^{210}Po (Bq·kg^{-1})	
	Root	Above ground part of plant
	Area around retention reservoir	
Alopecurus pratensis	150.50 ± 4.97	23.21 ± 1.25
Lysimachia nummularia	108.55 ± 3.95	15.85 ± 0.58
	Area around pumping station	
Alopecurus pratensis	37.99 ± 2.52	20.09 ± 0.72
Lysimachia nummularia	37.44 ± 1.09	12.10 ± 0.79

from soil. The amounts of polonium are dependent on the polonium content in soils and dissoluble form of polonium in groundwater. The coincident research of transfer of natural radionuclides from soils to plant were conducted in south-western Spain [17, 19]. The polonium concentration in analyzed plant (*Spartina densiflora*) collected at the Odiel Marsh in February and November 1993 ranged widely from 2.16±0.23 mBq·g^{-1} to 42.6±2.7 mBq·g^{-1} for ^{238}U, 3.11±0.36 mBq·g^{-1} and 46.4±2.4 mBq·g^{-1} for ^{238}U, 5.74±0.48 mBq·g^{-1} and 45.2±4.5 mBq·g^{-1} for ^{210}Po [19]. In general, the highest concentrations in plants were found in areas, where the concentrations of radionuclides in soil were the highest, too. The levels of ^{210}Po and uranium ^{234}U were similar, but higher amounts of uranium ^{238}U were in samples of *Spartina densiflora* and *Spartina maritima* collected in 1996: 5.58±0.41–50.1±2.4 mBq·g^{-1} for ^{210}Po, 2.37±0.20–42.6±2.7 mBq·g^{-1} for ^{234}U and 30.7±7.3–877±19 mBq·g^{-1} for ^{238}U, 5.05±0.41–40.6±1.1 mBq·g^{-1} for ^{210}Po, 3.01±0.42–49.6±3.1 mBq·g^{-1} for ^{234}U, 46.8±7.4–877±19 mBq·g^{-1} for ^{238}U. The maximum radionuclides concentrations was obtained in samples covered by water for a longer period [17]. Also the enhanced radioactivity of polonium lead, radium was observed in the marsh from area located in the vicinity of a phosphoric acid production complex in south-western Spain [18].

Conclusion

In this work we present results of a study concerning the distribution of natural radionuclides ^{210}Po, ^{234}U and ^{238}U in water, phosphogypsum and plants (yellow oat-grass, meadow foxtail, moneywort) samples collected around the phosphogypsum waste heap at Wiślinka. Polonium ^{210}Po concentrations were found to vary between 7.08±0.52 mBq·dm^{-3} and 165.7±1.4 mBq·dm^{-3} in water samples from the Martwa Wisła and area around the phosphogypsum dump, respectively. The unexpectedly wide variations of uranium concentration were observed in the waters of reservoir what indicates that this radionuclide is lixiviated from the phosphogypsum waste dump to the retention reservoir water. During the production of phosphoric acid, uranium distributes into the produced acid, but most of polonium gets into phosphogypsum. The lower concentration of uranium and polonium radionuclides in water from the Martwa Wisła river indicated that the process of their release to the Wisła river water is not significant. The results explain the environmental origin of uranium and polonium in water and plant. The radionuclides of polonium and uranium were found in deciduous, exposed to weather conditions leaves. The major sources of polonium and uranium in plants are wet and dry atmospheric falls gathering soil and air dust from the phosphogypsum waste dump. The highest polonium concentration was found in the near-ground plant parts. However, the most important source of radionuclides in plants is the root system. Polonium concentration in the root of two selected plants was six times higher than in the other plant parts. Significant meaning has the sort of solum substratum. The areas of reservoir retention have a much higher concentration of radionuclides than the pumping station area. The amount of polonium depends on its concentration in soil and the content of dissoluble forms of polonium in groundwater. The results indicate that the Phosphoric Fertilizers Industry of Gdańsk has enormous impact on the differentiated content of radionuclides in plants in the vicinity.

Acknowledgment. The authors would like to thank the Polish Ministry of Higher Education and Sciences for the financial support of this work under grant: DS-8460--4-0176-9 and BW/8000-5-0249-9.

References

1. Alcaraz Pelegrina JM, Martinez-Aguirre A (2001) Natural radioactivity in groundwaters around a fertilizer factory complex in south of Spain. Appl Radiat Isot 55;419–423
2. Al-Masri MS, Al-Bich F (2002) Polonium-210 distribution in Syrian phosphogypsum. J Radioanal Nucl Chem 251;3:431–435
3. Azouazi M, Ouahidi Y, Fakhi S, Andres Y, Abbe JCh, Benmansour M (2001) Natural radioactivity in phosphates, phosphogypsum and natural waters in Morocco. J Environ Radioact 54;231–242
4. Bagatti D, Cantone MC, Giussani A *et al.* (2003) Regional dependence of urinary uranium baseline levels in non--exposed subjects with particular reference to volunteers from Northern Italy. J Environ Radioact 65;3:357–364
5. Baturin GN (1975) Uran v sovremennom morskom osadkoobrazovanii. Moskva, Atomizdat, p 152
6. Bolivar R, García-Tenorio M, García-León J (1996) On the fraction of natural radioactivity in the production of phosphoric acid by the wet acid. Radioanal Nucl Chem 214;2:77–88
7. Boryło A, Nowicki W, Skwarzec B (2009) Isotopes of polonium ^{210}Po, uranium ^{234}U and ^{238}U for industrialized areas (Wiślinka) in Poland. J Environ Anal Chem 89;8–12
8. Bou-Rabee F, Bakir Y, Bem H (1995) Contribution of uranium to gross alpha radioactivity in some environmental samples in Kuwait. Environ Int 21;3:293–298
9. Browne E, Firestone FB (1986) Table of radioactive isotopes. Shirley VS (ed). Wiley, New York
10. Brzyska W (1987) The lanthanide and actinide. Wydawnictwo Naukowo-Techniczne, Warsaw (in Polish)
11. Harada K, Burnet WC, Cowart JP, Larock PA (1989) Polonium in Florida groundwater and its possible relationship to the sulfur cycle and bacteria. Geochim Cosmochim Acta 53:143–150
12. http://epa.gov/safewater/radionuclides/index.html

13. Hull CD, Burnett WC (1996) Radiochemistry of Florida phosphogypsum. J Environ Radioactiv 32;3:213–238
14. Hurst JF, Arnold WD (1982) A discussion of uranium control in phosphogypsum. Hydrometallurgy 9:69–82
15. Industrial using of phosphogypsum, http://www.polski-gips.pl/index.php?id=125
16. Jahnz A (2007) The inflow of polonium, uranium and plutonium from the Vistula River catchment area to the Baltic Sea. PhD Dissertation. Faculty of Chemistry, The University of Gdańsk, Gdańsk
17. Martinez-Aguirre A, Garcia-León M (1996) Transfer of natural radionuclides from soils to plants in a wet marshland. Appl Radiat Isot 47;9/10:1103–1108
18. Martinez-Aguirre A, Garcia-León M (1997) Radioactive impact of phosphate ore processing in a wet marshland in southwestern Spain. J Environ Radioactiv 34;1:45–57
19. Martinez-Aguirre A, Garcia-Orellana I, Garcia-León M (1997) Transfer of natural radionuclides from soils to plants in a marsh enhanced by the operation of non-nuclear industries. J Environ Radioactiv 35;2:149–171
20. Meinrath A, Schneider P, Meinrath G (2003) Uranium ores and depleted uranium in the environment with a reference to uranium in the biosphere from the Erzgebrige/Sachsen, Germany. J Environ Radioactiv 64;175–193
21. Niesmiejanow AN (1975) Radiochemistry. Państwowe Wydawnictwo Naukowe, Warsaw (in Polish)
22. Pawuła A (1995) Environmental hazards due to radioactive contamination of water. Ochrona Środowiska 3;58:23–28 (in Polish)
23. Periáñez R, Martinez-Aguirre A (1997) Uranium and thorium concentrations in an estuary affected by phosphate fertilizer processing: experimental results and a modeling study. J Environ Radioactiv 35;3:281–304
24. Periáñez R, Martinez-Aguirre A, Garcia-León M (1996) U and Th isotopes in an estuarine system in southwest Spain: tidal and seasonal variations. Appl Radiat Isot 47;9/10:1121–1125
25. Rutherford PM, Dudas MJ, Samek RA (1994) Environmental impacts of phosphogypsum. Sci Total Environ 99:1–38
26. Sam AK, Ahmed MMO, El Khangi FA, El Nigumi YO, Holm E (1999) Radiological and chemical assessment of Uro and Kurun rock phosphates. J Environ Radioactiv 42;1:65–75
27. Sam AK, Holm E (1995) The natural radioactivity in phosphate deposits from Sudan. Sci Total Environ 162;173–178
28. Saueia CH, Mazzilli BP, Favaro DIT (2005) Natural radioactivity in phosphate rock, phosphogypsum and phosphate fertilizers in Brazil. J Radioanal Nucl Chem 264;2:445–448
29. Silva NC, Fernandes EAN, Cypriani M, Taddei MHT (2001) The natural radioactivity of Brazilian phosphogypsum. J Radioanal Nucl Chem 249;1:251–255
30. Skwarzec B (1995) Polonium, uranium and plutonium in the southern Baltic ecosystem. Rozprawy i Monografie Instytutu Oceanologii PAN, Sopot (in Polish)
31. Skwarzec B (1997) Polonium, uranium and plutonium in the southern Baltic Sea. Ambio 26;2:113–117
32. Skwarzec B (1997) Radiochemical methods for the determination of polonium, radiolead, uranium and plutonium in environmental studies. Chem Anal (Warsaw) 42:107–115
33. Skwarzec B, Boryło A, Strumińska DI (2002) ^{234}U and ^{238}U isotopes in water and sediments of the southern Baltic. J Environ Radioactiv 61;3:345–363
34. Skwarzec B, Boryło A, Strumińska DI (2004) Activity disequilibrium between ^{234}U and ^{238}U isotopes in southern Baltic. J Water, Air Soil Pollut 159;1:165–173
35. Skwarzec B, Strumińska DI, Boryło A (2006) Radionuclides of iron (^{55}Fe), nickel (^{63}Ni), polonium (^{210}Po), uranium (^{234}U, ^{235}U, ^{238}U) and plutonium (^{238}Pu, $^{239+240}$Pu, ^{241}Pu) in Poland and Baltic Sea environment. Nukleonika 51;45–51
36. Szymański W (1996) Nuclear chemistry. The outline of radioactive transformation issues. Państwowe Wydawnictwo Naukowe, Warsaw (in Polish)
37. Upchurch SB, Oural CR, Foss DW, Brookor HR (1991) Radiochemistry of uranium series isotopes in ground water. FIPR Pub. No. 05-022-092
38. WHO, Guidelines for drinking water quality, 3rd ed. www.who.int/water_sanitation_health/dwq/gdwq0506_9.pdf